United States Court of Appeals
for the
District of Columbia Circuit

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DISTRICT OF COLUMBIA
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BRIEF AND APPENDIX FOR APPELLANT

IN THE

United States Court of Appeals

FOR THE DISTRICT OF COLUMBIA.

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No. 8472

MONSANTO CHEMICAL COMPANY, A CORPORATION, *Appellant*,

v.

CONWAY P. COE, COMMISSIONER OF PATENTS,
Appellee.

Appeal from the District Court of the United States for the District of Columbia.

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FOR THE DISTRICT OF COLUMBIA.

No. 8472.

MONSANTO CHEMICAL COMPANY, *Appellant,*

v.

CONWAY P. COE, Commissioner of Patents, *Appellee.*

BRIEF FOR APPELLANT.

JURISDICTIONAL STATEMENT.

This is an appeal from a decision of the District Court of the United States for the District of Columbia dismissing a complaint brought by Monsanto Chemical Company, Charles B. Durgin, Robert N. Foster and Charles F. Booth against Conway P. Coe in his official capacity as Commissioner of Patents of the United States Patent Office, for the issuance of a patent on an application of said Durgin, Foster and Booth, assignors of the entire right, title and interest in said application and the invention described therein to said Monsanto Chemical Company. This appeal is brought by Monsanto Chemical Company as the real party in interest.

The District Court had jurisdiction of the complaint under the provisions of the Revised Statutes, Section 4915; U. S. C., Title 35, Sec. 63 (Complaint, paragraph 1, App. p. 2). This Court has jurisdiction of this appeal under the provisions of U. S. C., Title 28, Sec. 225a.

STATEMENT OF THE CASE.

The complaint requests that the Commissioner of Patents be directed to issue a patent to plaintiffs upon an application for Letters Patent Serial No. 733,392 for improvements in "Soluble Dehydrated Sodium Phosphates and Process for Producing Same", filed in the United States Patent Office on July 2, 1934 as a continuation-in-part of a prior application Serial No. 438,955, filed March 26, 1930. The complaint is particularly directed to claims 34 to 39, 67, 68 and 69 of said application Serial No. 733,392 (App. pp. 2-6). The action was discontinued as to claim 69 by plaintiffs at the trial.

The invention involved relates to a process for the softening of water by adding thereto reaction products obtained by the fusion together and reaction of tetrasodium pyrophosphate ($Na_4P_2O_7$) and sodium metaphosphate ($NaPO_3$) and particularly to such reaction products designated as "a water soluble salt of tetraphosphoric acid, $H_6P_4O_{13}$" (claims 34 to 39) and as "sodium triphosphate, $Na_5P_3O_{10}$" (claims 67 and 68).

Claims 34 to 39 are identical with the claims of U. S. Patent No. 2,059,570 to Fiske et al., (App. p. 61), issued on an application filed December 7, 1934, and were inserted in the application in suit for the purpose of interference proceedings with that patent.

After entry of claims 34 to 39 in the application, an interference was declared between the application and the Fiske et al. patent (Interference No. 73,850) which was eventually dissolved on motion of the patentees on the ground that applicants could not make the claims of the interference since they included matter which had no proper basis in the original specification (Examiner's Statement, App. pp. 139-140).

Claims 67 and 68 are directed to the softening of hard water by the addition thereto of sodium triphosphate ($Na_5P_3O_{10}$).

Claim 69 is generic to the other claims in issue and defines a process in which a water soluble polyphosphate is added to hard water.

The allowed claims 62 to 65 (App. pp. 91-92) are directed to treatment of hard water with fused reaction products of sodium metaphosphate and tetrasodium pyrophosphate, or of monosodium and disodium orthophosphate, or of soda ash and orthophosphoric acid, in proportions within the range equivalent to ratios of sodium metaphosphate to sodium pyrophosphate of from 1 to 1 to 1 to 4. Allowed claim 66 is similar to allowed claim 65 except that the range of ratios is from 1 to 4 to 4 to 1.

All the claims referred to above were finally rejected by the Examiner as unpatentable over the following prior patents and publications:

Tanner	123,743	Feb. 13, 1872
Precht	502,424	Aug. 1, 1893
Hall et al.	1,903,041	March 28, 1933
Hall	1,956,515	April 24, 1934
Precht, British	7,958	Feb. 25, 1893

The Polyphosphates, N. Parravano, G. Calcagni, Zeitschrift Fur Anorganische Chemie, Vol. 65 (1910), pp. 1 to 9

Gmelin's Handbuch, 8th Ed., Vol. Sodium (1927), pp. 924-5

Claims 34-39 and claims 67-69 were additionally finally rejected by the Examiner on the ground that there is no basis in the original specification for these claims. Claims 62-66 were further rejected on the ground that there is no sufficient basis in the original specification to support the range of proportions recited in the claims.

In the decision of the Board of Appeals of April 21, 1941 (App. pp. 145-150), the Examiner's rejection of claims 34-39 and 67-69 was affirmed on the ground that the specification did not disclose the "specific constituents" defined by these claims.

The Board of Appeals reversed the Examiner's rejection of claims 62-66 both as to patentability over the prior art and as to basis for the claims in the specification.

Supplemental decisions of the Board of Appeals were rendered on May 5, 1941 (App. p. 150) and on May 28, 1941 (App. p. 151) to correct errors in nomenclature.

In appellee's answer to the complaint, appellee relied on the reasons given by the Examiner in his statement and by the Board of Appeals in its decisions of April 21, 1941, May 5, 1941, and May 28, 1941.

Appellant's testimony before the District Court was directed to showing the identity of the compositions disclosed in the application with the substances designated in the claims in issue and to showing the novel and distinctive advantages of using as water softening agents the water soluble salts of tetraphosphoric acid, $H_6P_4O_{13}$ (claims 34-39) and sodium triphosphate, $Na_5P_3O_{10}$ (claims 67 and 68)—both of which are obtained by the fusion together of tetrasodium pyrophosphate and sodium metaphosphate.

No testimony was taken on behalf of appellee.

The District Court dismissed appellant's complaint, holding that the application as filed did not contain a disclosure of the use of a salt of tetraphosphoric acid or of sodium triphosphate for the softening of water, and holding it would not require invention in view of the Hall patents 1,903,041 or 1,956,515 and in view of the prior publications cited in the findings to use alkali metal triphosphates or tetraphosphates for softening water. (App. pp. 153-154)

Appellant contends that the decision of the District Court is erroneous, as a matter of law, because of the substantially conclusive and uncontradicted evidence offered by appellant as to the identity of the substances disclosed in the application with the substances designated as salts of tetraphosphoric acid and as sodium triphosphate in the claims in issue, and because the holding of lack of invention is inconsistent with the evidence and with the decisions of the Board of Appeals and of the Commissioner of Patents.

STATEMENT OF POINTS RELIED ON.

1. Appellant contends that the District Court erred in not finding that the uncontradicted testimony and evidence offered by appellant showed beyond any reasonable doubt that the substances disclosed in the application are identical with the substances designated in the claims in issue as salts of tetraphosphoric acid and as sodium triphosphate.

2. Appellant contends that the District Court erred in holding that it would not require invention in view of the Hall patents and the publications cited in the findings of the Court to use alkali metal triphosphates or tetraphosphates for softening water, and particularly, that in so holding the Court erred in not giving due weight to the decision of the Board of Appeals holding such subject matter to be inventive and to the action of the Commissioner of Patents in granting a patent to another for the same invention.

SUMMARY OF ARGUMENT.

Appellant's application as filed contained a proper basis for the claims in issue because appellant has shown beyond a reasonable doubt by uncontroverted and unquestioned evidence that the substances described in the application as filed as advantageous for the softening of water are identical with the substances known in the chemical art as salts of tetraphosphoric acid and as alkali metal triphosphates. Appellants are entitled to use, as designations for the substances described by them, names which are used by those skilled in the chemical art to designate those substances, even though the names were not originally used in the application as filed.

It was an act of invention to use alkali metal tetraphosphates and triphosphates for the softening of water in spite of the prior suggestion of the use for this purpose of some of the raw materials which are used in the fusion process to make alkali metal tetraphosphates and triphosphates. It could not have been foreseen by those skilled in the art that the alkali metal tetraphosphates and triphosphates are much more effective in the softening of water than sodium metaphosphate and tetrasodium pyrophosphate. The latter two substances must be fused together at high temperatures (above at least 550° C.), to make sodium tetraphosphate and sodium triphosphate which applicants use as water softening agents. That applicants' disclosures amount to invention was found by the Board of Appeals in allowing to applicants claims broader than the claims in issue and was recognized by the action of the Commissioner of Patents in allowing to the patentees of U. S. Patent No. 2,059,570 claims identical with claims 34 to 39 in issue.

The Nature of the Invention.

The invention is based upon the discovery by applicants that by the fusion together of tetrasodium pyrophosphate ($Na_4P_2O_7$) and sodium metaphosphate ($NaPO_3$), reaction products are obtained which have greatly enhanced water softening properties over mere mechanical mixtures or unreacted mixtures of tetrasodium pyrophosphate and sodium metaphosphate. The curve designated as "G" of Figure 5 of the application as filed (App. p. 89) shows the minimum temperatures at which various mixtures of sodium pyrophosphate and sodium metaphosphate must be heated before they fuse and react to form the products applicants use as water softening agents.

Instead of starting with tetrasodium pyrophosphate ($Na_4P_2O_7$) and sodium metaphosphate ($NaPO_3$), equivalent proportions of raw materials which readily react under the conditions of the fusion process to form tetrasodium pyrophosphate ($Na_4P_2O_7$) and sodium metaphosphate ($NaPO_3$) may be used. For example, the products having the enhanced water softening properties discovered by applicants may also be prepared by reacting in proper proportions (1) mixtures of monosodium and disodium orthophosphates ($NaH_2PO_4 + Na_2HPO_4$) or (2) by reacting sodium carbonate and orthophosphoric acid ($Na_2CO_3 + H_3PO_4$).

The Disclosure of the Application.

Applicants first disclosed the use of fusion products of pyro and metasodium phosphates or their equivalents for the treatment of water in their application Serial No. 438,955, filed March 26, 1930. The present application was filed July 2, 1934 as a continuation-in-part of the earlier application (Defendant's answer, paragraph 4, App. p. 7).

The specification disclosed the production of improved compounds for the treatment of water by melting together tetrasodium pyrophosphate ($Na_4P_2O_7$) and sodium metaphosphate ($NaPO_3$) and thereafter rapidly cooling the fusion product. (App. p. 74)

In Example 1, 76.5 pounds of monosodium orthophosphate ($NaH_2PO_4.2H_2O$) and 134.7 pounds of disodium orthophosphate ($Na_2HPO_4.12H_2O$), theoretically equivalent to 50 per cent tetrasodium pyrophosphate and 50 per cent sodium metaphosphate, were heated to the melting point of the mixture at approximately 620° C. (App. p. 75)

In Example 2, 74.14 pounds of sodium carbonate and 78.26 pounds of phosphoric acid (H_3PO_4) equivalent to a theoretical composition consisting of 80 per cent tetrasodium pyrophosphate and 20 per cent sodium metaphosphate, were heated gradually to the melting point at approximately 940° C. (App. p. 76)

The drawings of the application (App. pp. 89-90) show the properties of the fused compound over the complete range of ratios of equivalent tetrasodium pyrophosphate and sodium metaphosphate and show the production of mixtures varying by 10 per cent differentials from 90 parts of metaphosphate to 10 parts of pyrophosphate to 10 parts of metaphosphate to 90 parts of pyrophosphate.

Appellant's Exhibit 1 (App. p. 41) clearly shows the extent of the original disclosure and the scope of the claims in issue. This exhibit is identical with Fig. 5 of the application as filed except for the added shading and color. This chart shows the melting points of fusion products of sodium pyrophosphate ($Na_4P_2O_7$) and sodium metaphosphate ($NaPO_3$) or their equivalents, including at either end of the curve the melting points of the individual starting materials. The shaded portion of the chart indicates the range of compositions covered by the claims allowed by the Board of Appeals.

The range colored yellow indicates the compositions referred to in the literature as sodium tetraphosphate (the subject matter of claims 34 to 39). The range colored orange indicates the compositions referred to in the literature as sodium triphosphate (the subject matter of claims 67 and 68).

The Subject Matter of the Claims is Disclosed in the Application.

The testimony of the witness Reynolds which was not contradicted or questioned by the appellee shows beyond any possible doubt

1) that the methods described in the application for producing the fusion products used by applicants for water softening are identical with the methods described in the chemical literature for producing sodium tetraphosphate and sodium triphosphate; and

2) that the products obtained by the methods described in the application are identical with the substances designated in the chemical literature as sodium tetraphosphate and sodium triphosphate.

This testimony was based on the testing by the witness by chemical and physical tests, including X-ray examination, of substances produced in accordance with the disclosures of the application and of the chemical literature, as well as upon his personal examination of and familiarity with the chemical literature.

The conclusions as to identity of the products described in the application with the substances known as sodium tetraphosphate and triphosphate, drawn by the witness from the experiments and tests which he described in his testimony, were so obviously correct that they were not questioned by the attorney for the Commissioner of Patents.

Identity of Applicants' Methods With Prior Art Methods of Making Tetraphosphates and Triphosphates.

Appellant's Exhibit 2 (App. p. 43) is a translation from Dammer's Handbuch Der Anorganischen Chemies (Handbook of Inorganic Chemistry) 1894, Vol. 2, pages 124 and 125. This shows that the sodium salt of tetraphosphoric acid may be formed by melting together sodium metaphosphate ($NaPO_3$) and sodium pyrophosphate ($Na_4P_2O_7$), or by melting together the sodium metaphosphate with trisodium phosphate (Na_3PO_4) or by melting together sodium hexametaphosphate ($Na_6P_6O_{18}$) with pyrophosphate or orthophosphate.

Appellant's Exhibit 3 (App. p. 44) is a translation of a portion of an article by Parravano and Calcagni in Zeitschrift für Anorganischen Chemie (Journal of Inorganic Chemistry) Vol. 65, 1910, including equations for the reaction of sodium pyrophosphate and sodium metaphosphate to form sodium tetraphosphate and sodium triphosphate according to the proportions of starting materials.

By referring to Figure 5 of the application, which figure corresponds to appellants' Exhibit 1 (App. p. 41) except for the shading, it will be seen that applicants disclosed the minimum fusing points or melting points of the various mixtures of sodium metaphosphate ($NaPO_3$) and sodium pyrophosphate ($Na_4P_2O_7$) used to make these improved water softening agents. The portion of Exhibit 1 colored yellow represents the mixtures of sodium metaphosphate ($NaPO_3$) and sodium pyrophosphate ($Na_4P_2O_7$) which may be used as raw materials to make sodium tetraphosphate, and this exhibit also shows the temperature to which the mixture of raw materials must be heated to fuse or melt them. Likewise, that portion of Exhibit 1 colored orange represents the mixtures of the same raw materials which may be used to make sodium triphosphate as well as the temperatures to which these mixtures of raw materials must be heated to fuse or melt them. It is clear that applicants' disclosure is identical with the teachings of the prior art for the preparation of sodium tetraphosphate or the alkali metal salt of tetraphosphoric acid and sodium triphosphate.

Additional statements are found in the other chemical literature in evidence (Appellant's Exhibits 4 and 5, App. pp. 44-51).

For example, in the extract from Mellor's Inorganic and Theoretical Chemistry, 1928, Vol. VIII (App. pp. 49-50) there is described the production of sodium triphosphate by fusing a mixture of 100 parts of sodium pyrophosphate with 50 parts of sodium metaphosphate at a "bright red heat". "Bright red heat" is a temperature of from 850° C. to 950° C. The proportion of the reacting materials given in Mellor is substantially identical with the point marked 70/30 on Fig. 5 of the application and is within the area colored orange in appellant's Exhibit 1 (App. p. 41).

Other disclosures in the application as filed, which are identical in substance with the methods given in the chemical literature of record for the preparation of alkali metal triphosphates and tetraphosphates, are found in Example 1 of the specification (App. p. 75) showing the preparation of a product corresponding to a 50/50 ratio of pyro- and metaphosphates by fusing and reacting together at 620° C. mono-sodium orthophosphate (NaH_2PO_4) and di-sodium orthophosphate (Na_2HPO_4); in Example 2 of the specification (App. p. 76) showing the preparation of a product corresponding to an 80/20 ratio of pyro- and meta-phosphates by fusing and reacting together at 940° C. sodium carbonate (Na_2CO_3) and phosphoric acid (H_3PO_4); and in the specification at page 82 of the Appendix where reference is made to products corresponding to 60/40, 40/60 and 20/80 ratios of pyro- to meta-phosphates.

The identity of these methods with those described in the application as to materials, proportions and conditions is obvious, and the conclusions expressed by the witness (App. pp. 17-18) that the methods of preparation of the products which Durgin et al. disclosed for use in softening water are the very methods which the scientific literature disclosed for the production of sodium tetraphosphate and sodium triphosphate are correct beyond any reasonable doubt.

A summary of the chemical reactions involved in these methods is presented in Appellant's Exhibit 6 (App. p. 53) which is explained by the witness in his testimony (App. pp. 19-20).

Identity of Applicants' Fusion Products With Products Known to the Art as Tetraphosphates and Triphosphates.

That the fusion products disclosed in the application are identical with the products known in the chemical literature—some of which are referred to above—as sodium tetraphosphate and sodium triphosphate not only follows from the identity of the methods of production, but is additionally proved by direct chemical and physical comparison of products made according to applicants' disclosure with products made by the methods of the literature and with products sold under these names.

The methods of making, analyses and tests, other than X-ray tests, of twenty-four samples of such products are summarized in Appellant's Exhibit 7 (App. p. 54). A diagram of the results of water softening tests on applicants' products prepared by fusion as well as the prior art products is shown in Appellant's Exhibit 8 (App. p. 55). Typical comparative X-ray diagrams of the products are shown in Appellant's Exhibits 9-13 (App. pp. 56-60).

Referring to Appellant's Exhibit 8, which shows diagrammatically the number of parts by weight of the test samples required to soften hard water in the standard testing procedure, it will be seen that the samples fall into four definite groups on the basis of their water softening properties. The numbers identifying the test samples of Exhibit 8 correspond to the numbered samples of Exhibit 7.

Points 1, 2, 3, 7, 8, 9, 13, 14, 15 and 25 (colored yellow in the exhibit) represent samples made in accordance with the teachings of the literature for the making of sodium tetraphosphate. Of these samples, at least 1, 2, 3, 13, 14 and 15 definitely correspond to the methods disclosed in the application. Point 27 (colored green) represents the data obtained with a commercial sample of sodium tetraphosphate. The close correspondence of all these samples in water softening properties is striking.

Points 19, 20 and 21 (pink) indicate the water softening properties of unfused mechanical mixtures of sodium pyro and metaphosphates of the same empirical compositions as the fused samples.

Points 4, 5, 6, 10, 11, 12, 16, 17, 18 and 26 (orange) represent samples made in accordance with methods disclosed in the chemical literature for the production of sodium triphosphate. Of these at least numbers 4, 5, 6, 16, 17, 18 and 26 correspond to methods disclosed in the application. Point 28 (green) represents a commercial sample of sodium triphosphate.

Points 22, 23 and 24 indicate the water softening properties of unfused mechanical mixtures of equivalent proportions of sodium pyro and metaphosphates.

The water softening tests not only show that the fused products are superior to the unfused or unreacted mixtures but that the sodium tetraphosphate and sodium triphosphate made in accordance with the methods of the prior art and appellant's application give the same results.

Referring to the X-ray diagrams, Exhibit 9 (App. p. 56) shows the identity of the products obtained by three different methods of making sodium tetraphosphate described in the chemical literature, at least two of which (3 and 15) are disclosed in the application.

Exhibit 10 (App. p. 57) shows the X-ray diagrams of two samples of sodium tetraphosphate of slightly different composition showing the persistence of the characteristic line structure.

Exhibit 11 (App. p. 58) shows the identity of samples of sodium triphosphate made in accordance with the methods of the chemical literature, at least three of which (6, 18 and 26) are also disclosed in the application.

Exhibit 12 (App. p. 59) shows the identity of line structure of two samples of sodium triphosphate of slightly different composition.

Exhibit 13 (App. p. 60) shows the difference between fused compositions (3) and unfused mixtures (21) of the same composition.

The witness Reynolds, who holds a degree of Doctor of Philosophy in Analytical Chemistry and who is particularly experienced in the use of X-ray equipment (App. p. 10) testified unequivocally on the basis of the data placed in evidence that the substances described by the applicants in the application as filed are the same materials as the substances known in the chemical art as sodium tetraphosphate and sodium triphosphate (App. p. 24).

This identity, so clearly established, between the materials disclosed by the applicants for softening water and the sodium tetraphosphate and sodium triphosphate in the chemical literature, entitles the applicants to use the latter names to describe their substances even though these specific names were not used in the original application.

In the case of *In re Gebauer-Fülnegg et al.,* 121 F. (2d) 505, the application was directed to compositions including a substance disclosed as a rubber resin identified only as "plioform" and "pliolite". Neither the composition of "plioform" and "pliolite", nor a method of preparing them, were disclosed in the original application. The court held, on the basis of affidavits filed in the application, that the products "plioform" and "pliolite" were on the market and were generally known to those skilled in the art of chemistry at the time the original application was filed by applicants. Claims defining the substances used in the invention by the method of making which was known in the art at the time of filing the application but not included in the original disclosure, were held proper.

In *Westinghouse Electric & Mfg. Co.* v. *Radio Corporation of America*, 24 F. Supp. 935, the original disclosure referred to a photoelectric element including a layer of alkali metal. The court held that it was proper to revise the description to refer to the alkali metal as being in the form of small globules in view of the evidence in the suit showing that it was well known to those skilled in the art at the date of filing the application that photoelectric layers of alkali metals were necessarily in the form of discrete particles.

In the present case, in view of the fact that the terms "alkali metal tetraphosphates" and "alkali metal triphosphates" had long been used at the time of filing the application to designate the products obtained by the methods described in the application, applicants are clearly entitled to use these designations in the definition of their invention.

The Subject Matter of the Claims Amounts to Invention Over the Prior Art.

Both the Board of Appeals of the Patent Office in their decisions in the application in issue and the Commissioner of Patents in allowing the Fiske et al. patent 2,059,570 have clearly expressed the view that the subject matter of the claims in issue is inventive and not merely the expected skill of the "routineer". This view is fully supported by the testimony and evidence, as is clearly shown hereinafter.

The Unpredictable Advantages of Tetraphosphates and Triphosphates as Water-Softening Agents.

The striking superiority of the alkali metal tetraphosphates and triphosphates over mixtures of pyro- and metaphosphates in the softening of water is clearly shown in appellant's Exhibit 8 (App. p. 55). In this exhibit the mixtures are indicated by pink circles, and the tetra- and triphosphate compositions by yellow and orange circles, respectively. In each range of composition approximately twice as much of the unfused mixtures of pyro- and metaphosphates are required to soften water of standard hardness, as is required of the tetra- and tri-phosphates.

There is no suggestion of these facts in the prior patents or literature. The Hall patents, as stated in the findings of fact 8 and 9, disclose the use of alkali metal pyrophosphates and metaphosphates for the treatment of water. (It may be noted that Hall patent 1,956,515 was filed subsequent to the filing of applicants' parent application Ser. No. 438,955 and is therefore not a proper reference against the claims in issue.)

The prior publications referred to in findings of fact 10 and 11 describe the alkali metal triphosphates and tetraphosphates and methods of preparing them,—methods, incidentally, which are identical with the methods described by applicants for the preparation of the compositions used in the invention. Nowhere in the patents or literature of record is there any suggestion of the advantages of the alkali metal triphosphates and tetraphosphates for the softening of water.

The use in water softening of the alkali metal triphosphates and tetraphosphates would not be obvious to one skilled in the art for the reason that these products are only obtainable by reacting together by fusion the alkali metal metaphosphates and pyrophosphates and their equivalents (Reynolds, App. p. 36), and there was nothing to suggest to anyone that the fusion of these substances would result in products superior to mere unreacted mixtures of the substances. It might be said that knowing the use of the metaphosphates and pyrophosphates in water softening would suggest to one skilled in the art that *mixtures* of these substances would be likewise suitable, but there was nothing in the prior art to suggest to him the possibility that the costly operation of causing the substances to react together by fusion would result in an *improvement* in water softening properties over those of the mere mixtures. Those skilled in the art do not take obviously unnecessary steps. The fusion temperatures (Figure 5 of the application, App. p. 89) disclosed and used by applicants to make sodium tetraphosphate and sodium triphosphate from sodium metaphosphate ($NaPO_3$) and sodium pyrophosphate ($Na_4P_2O_7$) ranged from about 700-900° C. and these temperatures on the Fahrenheit scale correspond respectively to 1292° F. and 1652° F. Such temperatures are more than half the melting point of cast iron, which ranges from 2100° F. to 2200° F. Only to the mind of invention would occur the thought that the obviously unnecessary step of fusion might result in an enhancement of water softening properties. This conception could not be the result of reasoning alone as there are no data in the prior art suggesting any possibility of such improvement—nothing, in short, to lead the routine experimenter to try specific fusion products of meta and pyrophosphate for water softening in place of unfused mixtures of these materials. The routine experimenter does not try more expensive and less accessible materials which would seem to be at best mere equivalents of the readily available materials.

The Attitude of the Patent Office on the Question of Invention.

That the Board of Appeals of the Patent Office was convinced of the cogency of the foregoing arguments is abundantly clear from the decision of the Board in the application involved in this cause. In the decision of the Board of Appeals dated April 21, 1941, referring to claims 62 to 66 of the application, the Board stated (App. p. 149):

> "The Examiner has rejected the claims of this group on prior art which discloses the use of mixtures of metaphosphate and pyrophosphate for water-softening purposes and which also shows that it was known that sodium tetraphosphate and sodium triphosphate could be produced by fusing together suitable amounts of sodium metaphosphate and tetrasodium pyrophosphate. We are not satisfied that the substitution of these fusion products for mere mixtures of the starting materials from which such reaction products were produced was an obvious procedure, especially as the fused product appears to be considerably more efficient than the mixture itself".

Claims 62 to 66 of the application which the Board of Appeals was considering in the statement cited are directed to the use of a broad range of fused compositions including compositions corresponding to both the triphosphate and the tetraphosphate (App. pp. 91-92). Since the Board had before it all of the prior patents and literature cited by the Commissioner of Patents in his Answer (the references are listed in the opinion of the Board, App. p. 146), it is clear that the Board, which is the highest reviewing tribunal of the Patent Office on the question of invention, did not feel that the use of these substances was merely the expected routine of those skilled in the art.

In addition to the cited statement of the Board of Appeals and the action of the Board in allowing the broad claims of the application, the attitude of the Commissioner of Patents is clearly demonstrated by the granting of claims identical with claims 34 to 39 of the application in U. S. Patent 2,059,570 to Fiske et al. (App. p. 61).

A similar situation was presented to the Court of Customs and Patent Appeals in *In re Engelhardt,* 40 F. (2d) 760. This case was an appeal from the rejection by the Patent Office of claims identical with claims granted in a patent to one Barnebey. As the Court said:

> "The Patent Office has held these identical claims to be patentable and has issued a patent thereon to Barnebey, which patent is presumably valid". p. 764.

In the Engelhardt case the Board of Appeals had subsequently held the claims to be unpatentable in view of the prior art, which the Board of Appeals has not done in the case at bar. The Court said on this point:

> "Of course the issue of the Barnebey patent did not preclude the Patent Office from finding that the claims here in issue lack patentability. If the Patent Office was clearly wrong in finding patentability of the Barnebey application, it should not repeat its error with regard to the claims here involved, but we think that in such cases lack of patentability should very clearly appear to warrant rejection, and any doubt as to patentability should be more strongly resolved in favor of patentability than under circumstances where a patent had not been previously issued." p. 762.

In the instant case the failure of the Board of Appeals to uphold the Examiner's rejection of the claims for lack of patentability over the prior art and the Board's statement as to invention involved in the broader claims quoted above clearly present much stronger grounds for resolving any doubts in favor of patentability than were present in the Engelhardt case.

In holding that the claims should be allowed, the Court said:

> "No injustice can flow from the conclusion here reached. If, as a result of our action, an interference is declared with the Barnebey patent, and priority

> should be awarded to him, appellant will be eliminated. If priority should be awarded to appellant, a patent will issue to him and there will then be two patents outstanding upon the same invention. Under section 4918, Rev. St. (35 USCA sec. 66), the rights of the parties can be fully adjudicated in the federal courts, where expert witnesses can be produced, subject to cross-examination, and, if the court in such a proceeding should find that the process in issue is not patentable, both patents will be declared void, as the statute provides in such cases.'' p. 764.

The District Court was not faced with a decision of an administrative tribunal finding that the claims in issue did not involve invention, as in *Abbott* v. *Coe,* 109 F. (2d) 449, 71 App. D. C. 195, and other decisions of this Court to like effect. On the contrary, the administrative findings before the Court in the present appeal are explicit that there was invention. The allegation of the Commissioner of Patents in the Answer to the Complaint cannot be given the weight of an administrative finding, as to do so would throw the entire rule of law into hopeless confusion. Administrative findings are to be looked for in the record, not in the pleadings.

SUMMARY AND CONCLUSION.

The only ground relied on by the Board of Appeals for holding that applicants were not entitled to the claims in issue was that the claims were not supported by applicants' original disclosure in view of the doubt existing in the minds of the Board of Appeals whether the methods of the application would produce the tetraphosphates and the triphosphates of alkali metals.

A careful reading of the decision of the Board of Appeals can lead to no other conclusion but that the Board would have allowed the claims in issue if the record before the Board had shown as fully and unequivocally as the record before the District Court that the methods described in applicants' original specification produce the substances known in the chemical art as alkali metal salts of triphosphoric and tetraphosphoric acids.

In view of the findings of the Board of Appeals as to the existence of invention in the broader allowed claims, in view of the allowance by the Patent Office of claims identical with claims 34 to 39 to Fiske et al., and in view of the conclusive and uncontradicted evidence of record as to the identity of applicants' substances with the substances defined by the claims, it is respectfully submitted that the denial of the claims to appellant is unjust, inequitable and unlawful.

WHEREFORE, appellant urges that the judgment of the District Court be revised and reversed.

Respectfully submitted,

HAROLD T. STOWELL,
Attorney for Appellant.

J. RUSSELL WILSON,
HERBERT J. KRASE,
RALPH E. PARKER,
Of Counsel.

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IN THE

United States Court of Appeals

FOR THE DISTRICT OF COLUMBIA.

No. 8472.

MONSANTO CHEMICAL COMPANY, A CORPORATION, *Appellant*,

v.

CONWAY P. COE, COMMISSIONER OF PATENTS, *Appellee.*

Appeal from the District Court of the United States for the District of Columbia.

APPENDIX TO BRIEF FOR APPELLANT.

PLEADINGS, DOCKET ENTRIES AND OTHER PAPERS DESIGNATED BY APPELLANT.

1 In the District Court of the United States
For the District of Columbia

Civil Action No. 13279.

Monsanto Chemical Company, a corporation, 1700 South Second Street, St. Louis, Missouri, Charles D. Durgin, 1007 Montvue Road, Anniston, Alabama, Robert N. Foster, 1200 Forest Lane, Anniston, Alabama, and Charles F. Booth, 1029 Christine Avenue, Anniston, Alabama, *Plaintiffs,*

v.

Conway P. Coe, Commissioner of Patents, Washington, D. C., *Defendant.*

Complaint to Secure Issuance of Patent

To the Honorable Judges of the District Court of the United States for the District of Columbia.

The plaintiffs, for their complaint, allege:

1.

That the jurisdiction of this Court depends upon the Statutes of the United States relating to the grant and issuance of Letters Patent of the United States, and particularly upon that certain section thereof known as R. S. 4915; U. S. Comp. Stat. 1916, Sec. 9460; U. S. C., title 35, Sec. 63.

2 2.

That plaintiff, Monsanto Chemical Company, is a corporation of the State of Delaware, having a place of business at St. Louis, Missouri, and that plaintiffs, Charles B. Durgin, Robert N. Foster and Charles F. Booth, are citizens of the United States, and residents of Anniston, in the County of Calhoun, State of Alabama.

3.

That defendant, Conway P. Coe, is the Commissioner of Patents of the United States, a resident of the State of

Maryland, whose official residence as Commissioner of Patents is in the District of Columbia, and he is sued as Commissioner of Patents of the United States.

4.

That plaintiffs, Charles B. Durgin, Robert N. Foster and Charles F. Booth, did invent certain new and useful improvements in Soluble Dehydrated Sodium Phosphates and Process for Producing Same, for which invention an application for Letters Patent of the United States was filed in the United States Patent Office on July 2, 1934, entitled "Soluble Dehydrated Sodium Phosphates and Process for Producing Same" which application was given the Serial No. 733,392, being a continuation-in-part of a prior application for Letters Patent of the United States on said invention filed in the United States Patent Office by said plaintiffs on March 26, 1930, and given the Serial No. 438,955.

3 5.

That on the 6th day of October, 1941, the plaintiffs, Charles B. Durgin, Robert N. Foster and Charles F. Booth, by an instrument in writing, did sell, assign and transfer unto plaintiff Monsanto Chemical Company, the entire right, title and interest in and to said invention and in and to said application, whereby Monsanto Chemical Company was vested with the entire right, title and interest in said invention and application and any patent to be granted thereon.

6.

That said application was filed in accordance with the Laws of the United States and with the Rules of Practice of the Patent Office.

7.

That said application has been duly prosecuted in accordance with the Laws of the United States and with the Rules of Practice of the Patent Office.

8.

That a patent on the aforesaid application has been refused by the Commissioner of Patents, defendant herein.

9.

That the invention involved in this proceeding relates to the treatment of hard water by adding to the water a water-soluble polyphosphate, such as sodium triphosphate and sodium tetraphosphate, to prevent the deposition of an alkaline earth metal compound in the water.

4

10.

That said application has been passed upon by the Primary Examiner who refused to allow any of the claims of said application, and that the Primary Examiner finally rejected the following claims:

34. A process which comprises adding to hard water a water soluble salt of tetraphosphoric acid, $H.P.O_{13}$, so as to combine with an alkaline earth metal to prevent the deposition of an alkali earth metal compound therein.

35. A process which comprises adding to hard water a water soluble salt of tetra phosphoric acid, $H.P.O_{13}$, so as to combine with calcium to prevent the deposition of a calcium compound therein.

36. A process of softening water, which comprises decreasing the free ion concentration of an alkaline earth metal in hard water with a water soluble salt of tetra phosphoric acid, $H.P.O_{13}$.

37. A process of softening water which comprises decreasing the free ion concentration of an alkali earth metal in hard water with an alkali metal salt of tetra phosphoric acid, $H_6P_4O_{13}$.

38. A process of softening water which comprises decreasing the free ion concentration of calcium in hard water with a water soluble salt of tetraphosphoric acid, $H.P.O_{13}$.

5 39. A process of softening water which comprises decreasing the free ion concentration of calcium in

hard water with an alkali metal salt of tetraphosphoric acid, H.P.O.$_{13}$.

67. The process which comprises softening a hard water my adding to said hard water sodium triphosphate, $Na_5P_3O_{10}$.

68. The process which comprises softening a hard water by adding to said hard water a composition comprising the compound sodium triphosphate, $Na_5P_3O_{10}$, to prevent the deposition of an alkaline earth metal compound in said water.

69. A process which comprises adding to hard water a water-soluble polyphosphate so as to combine with an alkaline earth metal to prevent the depositian of an alkaline earth metal compound therein.

11.

That from the decision of the Primary Examiner an appeal was taken to the Board of Appeals of the United States Patent Office, which affirmed the rejection of the Primary Examiner in its decision dated April 21, 1941; and that no appeal has been taken to the United States Court of Customs and Patent Appeals from said decision.

12.

That the invention is new and useful and was not known or used by others in this country before the invention thereof by said Charles B. Durgin, Robert N. Foster and Charles F. Booth, and was not patented or described in any printed publication in this or any country before the invention thereof by said Charles B. Durgin, Robert N. Foster and Charles F. Booth, or more than two years prior to their said application for patent therefor, and not in public use or on sale in the Uunited States for more than two years prior to said application, and not patented in any country foreign to the United States on an application filed by said plaintiffs, Charles B. Durgin, Robert N. Foster and Charles F. Booth, or their legal representatives or assigns more than twelve months prior to said application for United States Letters Patent, and has not been abandoned.

Wherefore, the plaintiffs pray:

I. That this Honorable Court adjudge that plaintiffs, Monsanto Chemical Company, Charles B. Durgin, Robert N. Foster and Charles F. Booth, are entitled according to law to receive Letters Patent of the United States for the aforesaid invention as defined in claims 34 to 39 and 67 to 69, hereinbefore recited.

II. That this Honorable Court decree that the Commis-
sioner of Patents be directed to allow the aforesaid claims
34 to 39 and 67 to 69, and such other claims as upon
7 hearing the Court may find patentable, and to issue
to plaintiffs, Monsanto Chemical Company, Charles
B. Durgin, Robert N. Foster and Charles F. Booth, United
States Letters Patent containing said claims.

III. For such other and further relief as the nature of the case may require and as to this Honorable Court may seem meet.

MONSANTO CHEMICAL COMPANY
CHARLES B. DURGIN
ROBERT N. FOSTER
CHARLES F. BOOTH
By HAROLD T. STOWELL
Attorney for Plaintiffs
1319 F Street, Northwest
Washington, D. C.
Phone: Metropolitan 1147

Of Counsel:
J. RUSSELL WILSON,
St. Louis, Missouri.

* * * * * * * * * *

8 Endorsed: Filed Nov 25 1941 Charles E. Stewart, Clerk

Answer to the Complaint.

To the Honorable the Justices of the District Court of the United States for the District of Columbia.

1, 2, 3. Defendant admits the allegations of paragraphs 1, 2 and 3.

4. He admits that on July 2, 1934, plaintiffs Charles B. Durgin, Robert N. Foster and Charles F. Booth, claiming to have invented certain alleged new and useful improvements in Soluble Dehydrated Sodium Phosphates and Process for Producing Same, filed in the Patent Office an application for patent thereon, to which application Serial No. 733,392 was given. He admits that said application was a continuation in part of a prior application by said plaintiffs filed in the Patent Office on March 26, 1930, and given Serial No. 438,955.

9 5. He admits the allegation of assignment of said alleged invention and said application No. 733,392 to plaintiff Monsanto Chemical Company.

6, 7, 8. He admits the allegations of paragraphs 6, 7 and 8.

9. He admits that the alleged invention relates to the subject matter set out in paragraph 9.

10. He admits that plaintiffs' application was passed upon by the primary examiner who refused to allow and finally rejected claims 34 to 39, inclusive, and 67, 68 and 69 of said application. He admits that said claims are as set out in paragraph 10 except that in claims 34, 35, 36, 38 and 39 the formula "$H.P.O._{13}$" should $H_6P_4O_{13}$.

11. He admits the allegations of paragraph 11.

12. He admits that in said application Charles B. Durgin, Robert N. Foster and Charles F. Booth made averments corresponding to the allegations of paragraph 12, but denies that such allegations are sufficient to justify the issuance of a patent on said application containing any of

claims 34 to 39, inclusive, 67, 68 and 69 of said application since it is deemed that the said claims are unpatentable in view of the following prior patents and publications and for the reasons given in the statement of the examiner in answer to the appeal and the decisions rendered by the Board of Appeals on April 21, 1941, May 5, 1941, and May 28, 1941, copies of which will be furnished at the trial:

Tanner, 123,743, Feb. 13, 1872,
Precht, 502,424, Aug. 1, 1893,
Hall et al., 1,903,041, March 28, 1933,
Hall, 1,956,515, April 24, 1934,
Precht, British, 7,958, Feb. 25, 1893.

10 The Polyphosphates, N. Parravano, G. Calcagni, Zeitschrift Fur Anorganische Chemie, Vol. 65 (1910), pp. 1 to 9,

Gmelins Handbuch, 8th Ed., Vol. Sodium (1927), pp. 924-5.

Profert of copies of these patents and publications is hereby made.

W. W. COCHRAN
Solicitor, U. S. Patent Office,
Attorney for Defendant.

November 24, 1941.

I hereby certify that a copy of this Answer to the Complaint was mailed today, November 24, 1941, to the attorney for plaintiffs, Harold T. Stowell, 1319 F Street, N. W., Washington, D. C.

W. W. COCHRAN
Solicitor.

• • • • • • • • • •

11 Endorsed: Filed Dec 5 1941 Charles E. Stewart, Clerk

Stipulation of Counsel

It is hereby stipulated by and between the attorneys for the respective parties, as follows:

That in claims 34, 35, 36, 38 and 39 set out in paragraph 10 of the complaint the formula "$H.P.O._{13}$" should be $H_6P_4O_{13}$,

That the complaint be considered as amended in this respect, and

That the formula "$H.P.O_{13}$" in claims 34, 35, 36, 38 and 39 in paragraph 10 of the complaint be corrected to read $H_6P_4O_{13}$.

HAROLD T. STOWELL
Attorney for Plaintiffs
1319 F Street, N. W.
Washington, D. C.
W. W. COCHRAN
Attorney for Defendant
United States Patent Office
Washington, D. C.

Washington, D. C.,
December 1, 1941.

* * * * * * * * * *

TRANSCRIPT OF TESTIMONY.

14 Washington, D. C.,
Monday, November 16, 1942.

The above-entitled cause came on for trial before Edward C. Eicher, Chief Justice, at 10:00 o'clock a.m.

Appearances:

Harold T. Stowell,
J. Russell Wilson,
Herbert J. Krase, appearing on behalf of Monsanto Chemical Company.
E. L. Reynolds, appearing on behalf of the Commissioner of Patents.

15 **Dexter H. Reynolds** a witness for and on behalf of the plaintiffs, being first duly sworn, was examined and testified as follows:

Direct Examination

By Mr. Stowell:

Q. Mr. Reynolds, state your name, age and residence. A. Dexter H. Reynolds, age 40, residence 15 West Bowman Avenue, Dayton, Montgomery County, Ohio.

Q. What is your present position? A. Research chemist with Monsanto Chemical Company.

Q. Briefly outline to the court your technical education and experience. A. A.B. in chemistry, University of Missouri; Master of Science, Physical Chemistry, University of Arizona; Ph.D., Analytical Chemistry, University of Illinois.

16 I spent about four years with the General Electric X-ray Corporation in the technical development of X-ray equipment and its uses.

Since October 1939, I have been employed by Monsanto Chemical Company in my present connection.

Q. What has been your experience in the field of phosphate chemistry? A. Practically,—well, not practically, but the major portion of my work with Monsanto has been in phosphate chemistry.

Q. Are you familiar with the scientific literature relating to phosphates? A. Yes.

Q. And you read and translate the German language? A. Yes.

Q. Are you familiar with application No. 733,392 of Durgin, Foster and Booth, involved in this case? A. I am.

Q. Will you describe, briefly, the invention disclosed in that patent. A. This invention disclosed by Durgin, Foster and Booth, relates to the fusion of sodium pyrophosphate and sodium metaphosphate to form a material which has rather greatly enhanced water-softening properties over those of mixtures of the starting materials. It also discloses that other materials, other starting materials, than the pyrophosphates and metaphosphates of sodium may be used; for example, the monosodium phosphates, orthophosphates and the disodium orthophosphates in the proper proportions to give a final sodium to phosphorous ratio will give the same result.

17 Also starting with soda ash or sodium carbonate and phosphoric acid, orthophosphoric acid, we may arrive at the same end result.

Q. Those statements which you have just made are summaries of the disclosures in the Durgin, Foster and Booth application? A. I believe so; yes, sir.

Q. Is the fact that new substances may be prepared by fusion together of the sodium pyrophosphate and sodium metaphosphate, or of the equivalents that you have mentioned, a new fact with the Durgin, et al. application? A. No; it is not. Those preparations have been described in the literature many times over a great number of years.

The Court. What is the difference between "fusion" and "mixture"?

Mr. Stowell. A fusion brings about, in our opinion,—and I think you will see also in the opinion of the investigators, all of the scientific investigators,—a sort of reaction which produces a new chemical compound or series of chemical compounds.

These two materials, when fused together, are different materials than the mere mixture of them. There is a chemical reaction that takes place during that fusion process, and the resulting product, which we will show in considerable detail, is a different product in its chemical properties and in its physical properties, and in what may be called the fingerprints of chemical compounds, in the X-ray diagrams from the mechanical mixtures.

18 The Court. Well, the fusion mixture is a chemical process as distinguished from the physical process of mixing?

Mr. Stowell. It brings about a chemical process. Fusion is the condition required to cause the chemical reaction to take place.

By Mr. Stowell:

Q. Is that correct, Doctor? A. That is correct.

The Court. All right.

By Mr. Stowell:

Q. How have these products of the fusion, that is, pyrophosphate and metaphosphate, and their equivalents, been designated in the literature? A. These are known and have been known as the polyphosphates.

Q. Has the term sodium or alkaline, tetraphosphate or alkali metal salts of tetraphosphoric acid been used in the literature prior to this application? A. Yes; that designation has been used quite frequently to designate materials approximating a certain theoretical composition.

Q. What is the composition? A. In terms of the pyrophosphate and metaphosphate starting materials it would be between fifty and sixty parts of pyrophosphate and between forty and fifty parts of metaphosphate.

Q. Has the term sodium triphosphate or sodium salt of triphosphoric acid been used in the literature prior to this application? A. Yes. That term refers to a compo-
19 sition which would fall between seventy and thirty
parts of pyro- to the corresponding amounts of meta — no; from seventy to eighty parts of pyro-, and corresponding to that, twenty to thirty parts of meta—.

Q. Does any of the scientific or technical literature known to you prior to the filing date of the application of Durgin, et al., contain any suggestion of the water-softening properties of these materials, fusion products, or any suggestion of their use in the treatment of water? A. Not that I know of.

Q. Referring to the chart which I hand you, which is marked for identification as Plaintiff Exhibit No. 1,—the Court will find a copy of that chart as item No. 6 in the file,—this chart is identical with the Figure 5 of the Durgin, et al. application, is it not? A. It differs only in the appearance of colored shading on this one, which is not present on Figure 5 of Durgin's application.

Q. What does this chart indicate when taken in connection with the disclosure of the Durgin, et al., application? A. This chart shows the melting point of various mixtures of sodium pyrophosphate and sodium metaphosphate in proportions varying from zero to 100 percent in one direction and 100 percent to 0 in the other.

Mr. Stowell. I might say to your Honor that this particular figure has been selected as indicating possibly more clearly than anything we can say just what the controversy here is about, and if I may just joint out briefly, this curve, as the witness has stated, represents the melting-point curve of these fusion products which we have been discussing and which are disclosed in the Durgin, et al., application.

The Court. These degrees are Centrigrade on the chart, are they not?

The Witness. Yes, sir.

The Court. Up to 1000?

The Witness. Yes, sir.

The Court. All right.

Mr. Stowell. It is just one of the methods of identifying these materials. Incidentally, it shows in itself that we are dealing, at least, with new types of products because of the changes in the melting point from the starting materials.

Now, the shaded portion on the chart, starting from the 20 percent equivalent pyrophosphate and 80 percent equivalent metaphosphate on the left-hand side, and running to the reverse proportion on the other side, are the products which are covered by the allowed claims; the claims allowed by the Board of Appeals.

Any product within that range is within th escope, that is, the use of any of those products for water-softening is within the scope of the allowed claims.

The portion of the range which I have shaded yellow, we will show, is the range corresponding to what is known in the literature as tetraphosphates or salts of tetraphosphoric acid, which we are attempting to claim in the first group of claims.

The orange portion, which we have shaded orange, is in-
tended to indicate the composition known in the lit-
21 erature as triphosphates or salts of triphosphoric
acid and which are covered in the second group of
claims.

By Mr. Stowell:

Q. Are charts such as these commonly used to represent the properties of a series of compounds of varying compositions, Doctor? A. They are.

Q. What do the circle points along the line of the curve indicate to you? A. Those represent actual compositions which were used in determining data for this.

Q. Referring to this chart, what portion of it could be taken as indicating the composition referred to in the literature as sodium tetraphosphate or sodium salts of phosphoric acid? A. That range colored yellow between 50-50 and 60-40 compositions, since any composition within that range would contain, theoretically, at least 85 percent of the sodium tetraphosphate or sodium salts of tetraphosphoric acid.

Q. Theoretically 100 percent composition of the so-called sodium tetraphosphate would lie within that range, is that right? A. Yes; somewhere near the center of it.

Q. What portion of the chart, in your opinion, would indicate the substances referred to in the literature as sodium triphosphate or sodium salt of triphosphoric acid? A. That section colored orange on the chart, between 70-30 and 80-20 compositions, since again anything in that range would contain 85 percent of sodium triphosphate.

22 Mr. Stowell. I want to point out to your Honor
again, to clear up the situation, that this is, in fact,
part of the disclosure of the original Durgin, et al. application. We have only added some color to bring out our points, but the actual curve and the points on the curve are original disclosures in the application, that is, Figure 5 of

the Durgin, et al. application, so that aside from any color that we have given it physically, and by our remarks, it is original disclosure of the applicants.

The chart which the witness has just discussed is offered in evidence as Plaintiff Exhibit No. 1.

The Court. Any objection?

Mr. Reynolds. No, your Honor.

The Court. It may be admitted.

(The document identified as Plaintiff Exhibit No. 1 was admitted in evidence.)

By Mr. Stowell:

Q. I hand you a typewritten sheet marked "Translation from Dammers Handbuch Der Anorgan. Chemies, 1894, Vol. 2, Pages 124 and 125". Is that a correct translation of those pages cited? A. It is.

Q. What is the purport of the translated matter which appears? A. This states that according to previous workers the sodium salt of tetraphosphoric acid may be formed by melting together sodium metaphosphate, $NaPO_3$ and sodium pyrophosphate, $Na_4P_2O_7$, or by melting together the
metaphosphate with trisodium phosphate or by melt-
23 ing together sodium hexametaphosphate, $NaPO_3$,
taken six times, to form the sodium salt of tetraphosphoric acid.

Q. That is, the so-called hexametaphosphate may be melted with either the pyrophosphate, sodium pyrophosphate, or sodium orthophosphate to get the tetraphosphates. A. Yes. Those words are used.

Q. Then, isn't it a fact that the statement made in this scientific literature of the production of sodium salt of tetraphosphoric acid describes the same methods of producing the substances so named as are described in the Durgin, et al. application? A. That is correct.

Q. For the production of water-treating agents of that application. A. That is right.

Mr. Stowell. The translation which the witness has identified is offered in evidence as Plaintiff Exhibit No. 2.

The Court. It may be admitted.

(The document marked Plaintiff Exhibit 2 for identification was admitted in evidence.)

By Mr. Stowell:

Q. I hand you a typewritten sheet marked "Translation Parravano and Calcagni, 'Die Polyphosphate' Zeitschrift Fur Anorganische Chemie, Vol. 65, 1910, Page 3, lines 17 to 29." Have you compared that translation with the original and found it to be correct? A. I have.

Q. What is the substance of the translated items? A.
This describes the production of sodium triphos-
24 phate, sodium tetraphosphate and sodium decaphos-
phate, as examples of the polyphosphates, and states
the various types of polyphosphates obtained by fusing togethr pyro- and metaphosphates in varying proportions.

Q. Doctor, sometimes you use the term "fusion" and sometimes you use the term "melting together". Is there any distinction in those terms as you have used them? A. I believe not.

Q. They are both intended to mean the same thing; fusion and melting together? A. Yes, sir.

The Court. As the result of the application of heat.

The Witness. Yes; both resulting from the application of heat. When something is melted, it is fused; possibly a more elegant term, perhaps.

Mr. Stowell. The translation which the witness has testified to is offered in evidence as Plaintiff Exhibit No. 3.

The Court. It may be admitted.

(The document marked for identification as Plaintiff Exhibit No. 3 was admitted in evidence.)

Mr. Stowell. I hand you two pages marked for identification Plaintiff Exhibits 4-A and 4-B. Are these copies of pages 622 and 623 of "Inorganic Chemistry" by Ephraim published in 1926?

The Witness. That is right.

By Mr. Stowell:

Q. Is the purport of these pages substantially the same as that of the other literature references that you have testified to? A. It is.

25 Mr. Stowell. These sheets identified by the witness are offered in evidence as Plaintiff Exhibits Nos. 4-A and 4-B.

The Court. They may be admitted.

(The documents marked, respectively, Plaintiff Exhibits Nos. 4-A and 4-B were admitted in evidence.)

By Mr. Stowell:

Q. I hand you two sheets marked for identification as Plaintiff Exhibits 5-A and 5-B. Are these sheets copies of pages 990 and 991 of Inorganic and Theoretical Chemistry, by Mellor Vol. 8, published in 1928? A. That is right.

Q. Is the purport of these the same as the previous literature you testified to? A. That is right; very much in agreement.

Mr. Stowell. The exhibits identified by the witness are offered in evidence as Plaintiff Exhibits 5-A and 5-B.

The Court. They may be admitted.

(The documents marked, respectively, Plaintiff Exhibits Nos. 5-A and 5-B were admitted in evidence.)

By Mr. Stowell:

Q. What conclusions do you draw from these extracts from the scientific literature which have just been offered in evidence as to the preparation of the products designated as sodium tetraphosphate and sodium triphosphate? A. The conclusion appears obvious that they are prepared by the methods disclosed by the specifications of the
26 Durgin, et al. application; that they are produced by

fusing suitable proportions of sodium pyrophosphate and sodium metaphosphate or of materials which may give those products upon fusion; or, we might even define it separately so as to say any mixture of materials which, when fused, would give the composition corresponding to those salts, would result in their preparation.

Q. Is it correct, then, to say that the methods of preparation of the products which Durgin, et al. disclosed for use in softening water, are the very methods which the literature, scientific literature, discloses for the production of sodium tetraphosphate and sodium triphosphate? A. That is exactly right.

Q. Does the Durgin, et al. application disclose products prepared by fusion of the proper raw materials in the proportions indicated by the literature? A. Now, I didn't get that question straight.

(Whereupon, the pending question, as above recorded, was read by the reporter.)

A. (Continuing) Yes; in that they are in the proper range. That is seen by referring to Figure 5.

Q. Referring to Plaintiff Exhibit No. 1, do you find on that a disclosure of proportions corresponding to the proportions indicated in the literature? A. Yes.

Q. For these two products? A. The exact proportion would fall along the line connecting the point between the 50-50 composition, 60-40 in the case of the tetraphosphate and along the line between the 70-30 and 80-20 com-
27 positions for the triphosphate.

The exact compositions used by Durgin, which approximate those compositions, are the circle points at 50-50, 60-40, 70-30 and 80-20. 70-30 is almost the exact composition for the triphosphate; the exact theoretical composition, I should say.

Q. I hand you a sheet marked for identification as Plaintiff Exhibit No. 6. Your Honor will find this sheet as Item 13 in the file.

Will you explain briefly the contents of this sheet, Doctor? A. This sheet shows in chemical shorthand the chemical reactions involved in the present case.

In the first equation we have sodium carbonate, Na_2CO_3 which, reacting with orthophosphoric acid forms a compound which is known as monosodium phosphate, NaH_2PO_4.

The second equation shows the reaction between sodium carbonate and orthophosphoric acid to form disodium phosphate.

Q. Pardon me. The difference between those two equations, that is, the difference is based on a difference in proportion of the reactants? A. Yes.

Q. Which gives you a different product. A. In the first one, you have one molecule of sodium carbonate reacting with two molecules of acid to form two molecules of the monosodium phosphate, while in the second the ratio is one-to-one rather than one-to-two.

Equation 3 shows that the product of the first reaction, when heated, forms sodium metaphosphate, $NaPO_3$.

28 No. 4 shows that the product of the second reaction, when melted, forms sodium pyrophosphate.

Q. Pardon me. These chemical reactions represented by these four equations, are perfectly well-known and standard reactions? A. Very well-known and standard reactions.

Q. As a matter of fact, textbook chemistry? A. Yes.

No. 5 shows the reaction between one molecule of each of the reactants, products of 3 and 4, to form sodium triphosphate; the reaction taking place during the fusion.

No. 6 shows one molecule of sodium pyrophosphate reacting with two molecules of sodium metaphosphate to form sodium tetraphosphate.

Now, No. 7 shows the course of the reaction from the beginning, starting with sodium carbonate and phosphoric acid, to form the monosodium phosphate and the disodium phosphate which, when heated, will lose further water, to form sodium metaphosphate and sodium pyrophosphate which, upon fusion then reacts to form sodium triphosphate.

Reaction 7 is the chemists's method of representing all of the preceding reactions, and in this case No. 7 represents a summation of the first five reactions stated.

No. 8 likewise shows the course of the series reactions of one, two, three and four and six, occurring successively.

One could conclude from 7 and 8 that by starting at any point along that series of reactions, we would arrive at the same end product as indicated.

Q. In your opinion, does Equation 7 accurately
29 represent the reactions described in the chemical literature which you have just discussed? A. They do.

Q. Does it also accurately represent the reactions taking place in the methods disclosed in the Durgin, et al. application? A. They do.

Q. For the production of sodium triphosphate? A. They do.

Q. Are the same statements true of Equation 8 with respect to sodium tetraphosphate? A. They are.

Mr. Stowell. The sheet which the witness has just discussed is offered in evidence as Plaintiff Exhibit No. 6.

The Court. It may be admitted.

(The document marked for identification as Plaintiff Exhibit No. 6 was received in evidence.)

By Mr. Stowell:

Q. You have made a number of tests on materials made in accordance with the disclosure of the Durgin, et al. application and the disclosures of these literature references, have you not? A. Yes.

Q. Will you give an outline of the test samples which you have prepared and the tests which you have made on them?

Your Honor will find that No. 14 in the file. A. These test samples fall into four series, that is, four series of six samples each, and in each series the ratio of sodium metaphosphate to sodium pyrophosphate was varied from
30 a 50-50 mixture to an 80-20 mixture.

The first series used sodium metaphosphate and sodium pyrophosphate.

The second series used fused sodium metaphosphate, a form which is commonly termed in the literature as sodium hexametaphosphate and sodium pyrophosphate.

The third series started with disodium orthophosphate and monosodium orthophosphate.

The fourth series used sodium hexametaphosphate and sodium pyrophosphate.

Now, the first three series were fused and held at 950 degrees, for establishment of equilibrium, and then chilled as rapidly as was practical from that temperature.

The fourth series contributed simply a mechanical Mixture of sodium hexametaphosphate and sodium pyrophosphate.

In addition to those four series of samples, I have prepared one sample using sodium metaphosphate and sodium pyrophosphate, which was fused at 750 degrees and chilled from that temperature, instead of 950-degree fusion.

I prepared another sample, No. 26, from orthophosphoric acid and sodium carbonate. That was fused at 950 degrees and chilled from that temperature.

In addition, I examined two other samples, one designated as quadriphos or sodium tetraphosphate, from the American Cyanamide Company, and Sample No. 28, which is designated as sodium tripoly, which we have been terming triphosphate in this discussion, which was prepared by the Victor Chemical Works, but which I obtained from Calgon, Inc.

31 What tests were made on these samples? A. We analyzed each sample for its sodium oxide and phosphoric oxide content and determined the melting point, determined the pH of one per cent solution of all of them, and we conducted water-softening tests on all of them.

Q. Did you make X-ray diagrams of those samples? A. Yes. X-ray diagrams were prepared for each of them.

Q. All of these tests and X-ray diagrams were made by you or under your direct supervision? A. Yes.

Q. Is the sheet marked for identification Plaintiff Exhibit 7, which you have, a summary of the samples and the result which you obtained? A. It is.

Mr. Stowell. This sheet is offered in evidence as Plaintiff Exhibit No. 7.

The Court. It may be admitted.

(The document marked for identification as Plaintiff Exhibit No. 7 was admitted in evidence.)

By Mr. Stowell:

Q. State briefly what conclusions you draw from these test results, Doctor. A. The difference between fused samples, regardless of the starting materials used, and of the chemical mixtures of the staring materials, is best shown by the water-softening tests.

The Court. In the last column?

32 The Witness. Yes; that is the last column.

(Continuing) In those tests you will note that the first three samples of each series fall into a definite block.

Mr. Stowell. Pardon me.

By Mr. Stowell:

Q. I hand you a sheet marked for identification Plaintiff Exhibit No. 8.

The Court will find this sheet No. 15 in the file. A. On that sheet the numbers indicated with the yellow figures show the water-softening properties of those materials falling in the tetraphosphate range; that is, they constitute the water-softening results on the first three samples, of each of the first three series of samples. There are nine samples here.

Q. You are now referring to the group of indications in the lower left-hand portion of the chart, Doctor? A. Yes. Those in the lower left-hand portion colored in yellow. You notice that all samples in that group fall very close together there as to water-softening values.

The three numbers in red, blocked just above that, represent the mechanical mixture, or materials of the same composition as the fused materials shown below.

You will note that No. 27, which is the quadriphos sample, falls in that same range.

Q. That, I understand, represents what might be called commercial sodium tetraphosphate as obtainable today. A. That is so.

33 Now, the group of numbers colored orange, about the center at the right-hand side of the diagram, represent the results from the fused mixtures in the sodium triphosphate range.

The corresponding mechanical mixtures are represented in the block above that, numbered 22, 23 and 24, again colored in red.

This shows very definitely the superiority of the fused product over the mechanical mixtures in water-softening values, and shows that the values fall in the same range for each group as the range grouped around the tetraphosphate and the range grouped around the triphosphate.

Q. Dr. Reynolds, it is true, is it not, that the various samples indicated by the yellow circles on the water-softening test charts represent compositions in this range which is colored yellow in Plaintiff Exhibit 1? A. That is right.

Q. And are derived from the various starting materials which have been referred to in the literature? A. That is right.

Q. Including metaphosphate and pyrophosphate and monosodium and disodium orthophosphates? A. That is correct.

Q. In proper proportions throughout that range? A. That is right.

Q. And that the samples indicated by the orange circles in the water-softening test chart represent compositions throughout the range colored in orange on Plaintiff Exhibit 1? A. That is right.

34 Q. And represent also starting materials of all of the various natures referred to in the application? A. Yes, sir.

Q. And in the literature, is that right? A. Yes, sir.

Q. Now, referring to samples in what we have called the sodium tetraphosphate range, which are indicated by the yellow circles, is it your opinion, based on these and the other tests which you have made, that all of these samples are substantially the same material? A. They are.

Q. And that is the material known in the prior literature as sodium tetraphosphate or sodium salts of tetraphosphoric acid? A. That is right.

Q. Referring to the various samples indicated by the orange circles on the water-softening test chart, is it your opinion, based on these tests and the other tests which you have made, that all of those samples are substantially the same material and are the materials designated in the literature as sodium triphosphate or sodium salts of triphosphoric acid? A. That is my opinion.

Mr. Stowell. The chart which the witness has testified to is offered in evidence as Plaintiff Exhibit No. 8.

The Court. It may be admitted.

(The document marked for identification as Plaintiff Exhibit No. 8 was received in evidence.)

The Court. We will have a five-minute recess at this point.

35 (Whereupon a short recess was taken, after which the proceedings were resumed as follows:)

The Court. You may proceed.

By Mr. Stowell:

Q. On page 10 of the application of Durgin, et al., reference is made to a fused mixture containing the equivalent of 60 per cent of metaphosphate and 40 per cent of pyrophosphate. According to the table which is in evidence as Plaintiff Exhibit No. 7, your fused samples 3, 9 and 15, are all of the same equivalent compositions but are made, respectively, from monometaphosphate and pyro-, sodium pyrophosphate; hexametaphosphate and sodium pyrophosphate; and from mono- and disodium orthophosphates.

What do the X-ray diagrams indicate as to these samples, Doctor? A. They indicate that those three samples are identical.

Q. Have you a print of the X-ray diagrams of those three samples? A. I have; the pictures marked 3, 9 and 15.

Mr. Stowell. That would be item No. 16 in the file, your Honor. This print is offered in evidence as Plaintiff Exhibit No. 9.

The Court. It may be admitted.

(The documents referred to were marked Plaintiff Exhibit No. 9 and received in evidence.)

By Mr. Stowell:

Q. I might, to avoid any possible objection, ask you this: Did you make the original X-ray negatives from which these prints were made? A. I did.

36 Q. And these prints were made under your supervision? A. I made the prints myself.

The Court. Are those taken in the vertical position?

The Witness. No; these are X-ray diffraction diagrams.

By Mr. Stowell:

Q. Possibly a brief explanation of the meaning and procedure would be helpful. A. Well, we may have to go back quite a way to do that.

X-rays, as you know, are light rays of extremely short wave length. They are so short in wave length that they are invisible, yet they do have the power of penetrating otherwise opaque matter, as you are familiar with their use in medical diagnosis.

They also have the property, because of their various short wave lengths, of being scattered by atoms, which are all very small particles constituting matter in general.

Now, it is characteristic of the scattering of X-rays by matter that each particular substance scatters X-rays in a particular manner characteristic of that substance, so that we may make scattering patterns of X-rays from a series of different samples, and if those scattering patterns are identical, then the substances constituting the samples must be identical; that is, it is a finger-printing process.

If we made a set of finger prints from a known material, then at the same instant of the unknown, we know that the unknown is the same as the known material, so, from these three samples which were prepared from different starting materials, but ending with the same composition, we end up with three finger prints of the three materials; the
37 finger prints being identical proving identity of the samples themselves.

Q. Is this procedure and the technique that you have just described, standard procedure? A. Standard procedure, and it has been widely described in standard physical and mechanical literature and is accepted by the A. S. T. M. as a standard method of analysis.

Mr. Stowell. I might say that the original negatives, X-ray patterns of all these samples, are available for inspection by the attorney for the Patent Office if he cares to see them.

The Witness. I think you can see as much from the reproductions as you can from the original negative.

By Mr. Stowell:

Q. In the literature that you have previously referred to, investigators Fleitmann and Henneberg are frequently referred to as the original investigators to produce these materials known as sodium tetraphosphate, for example. Which, if any, of your samples is properly representative of the materials and the method of Fleitmann and Henneberg for making sodium tetraphosphate referred to in the prior literature. A. Sample 8, I believe, would come closest to their materials, in which I have used sodium hexametaphosphate and sodium pyrophosphate in the proportion of 56.6 pyro- to 43.4 meta-, which is the exact theoretical composition of the sodium tetraphosphate.

Q. What does the X-ray diagram of Sample No. 8 which

you prepared, according to the method of Fleitman
38 and Henneberg, indicate as compared with the
X-ray diagrams of Samples 3, 9 and 15 produced in
accordance with the method of the Durgin, et al. application? A. Again, identity is indicated, and this print—

Mr. Stowell. The witness is referring to the print marked for identification as Plaintiff Exhibit No. 10, which is Item 17 in the file.

The Witness. (Continuing) In Exhibit 10, the pattern or finger print for Sample No. 8 is compared with Sample No. 9, and is seen to be identical.

Mr. Stowell. The sheet containing the reproduction of patterns of samples Nos. 8 and 9 is offered in evidence as Plaintiff Exhibit No. 10.

The Court. It may be admitted.

(The document marked for identification as Plaintiff Exhibit No. 10 was received in evidence.)

By Mr. Stowell:

Q. One of the compositions specifically indicated on the diagrams of the Durgin, et al. application drawings is the equivalent composition of 80 parts of sodium pyrophosphate and 20 parts of sodium metaphosphate. Referring to your Exhibit 7, the test samples, samples of these compositions made from the various starting materials referred to in the Durgin, et al. application as well as in the prior art literature, are Nos. 6, 12, 18 and 26.

What do the X-ray diagrams indicate as to these samples? A. There again the patterns for Samples 6, 12, 18 and 26 show identity of the prepared material, regardless of starting materials used.

39 Mr. Stowell. That print is item No. 18.

The print just referred to by the witness is offered in evidence as Plaintiff Exhibit No. 11.

The Court. It may be admitted.

(The document referred to was marked Plaintiff Exhibit No. 11 and received in evidence.)

By Mr. Stowell:

Q. Would Sample No. 11 be illustrative of the material referred to in the literature as sodium triphosphate? A. It would, as the exact proportions of sodium pyrophosphate and sodium metaphosphate required by the theoretical formula for sodium triphosphate.

Q. What is indicated by the X-ray diagram of this sample? A. That, compared with the X-ray diagrams for 6, 12, 18 and 26, again shows identity.

Q. The sheet which you have shows what? A. Shows the diagram for 11 and 12, if held side by side.

Mr. Stowell. This print referred to by the witness is offered in evidence as Plaintiff Exhibit No. 12.

The Court. It may be admitted.

(The document referred to was marked Plaintiff Exhibit No. 12 and admitted in evidence.)

By Mr. Stowell:

Q. Some of your samples were unfused mixtures of starting materials in reacting mixtures? A. That is right; Samples Nos 19 to 24, inclusive.

Q. Are the X-ray diagrams of these unfused mixtures different from the X-ray diagrams of fused samples of the same nominal composition? A. They are different.

Q. I hand you print marked for identification Plaintiff Exhibit No. 13. What is that print? A. That is a print of the X-ray diagram for Sample No. 3 and for Sample 21.

Q. Pardon me. That is item No. 20.

Point out briefly the basis for your opinion as to the similarity or dissimilarity of these X-ray diagrams which you have been discussing. A. Of these particular two?

Q. Take those as an example. A. As I stated before, identity of X-ray diagrams indicates identity of materials; hence, differences in diagrams would indicate differences in materials.

You will note that there are lines present for No. 3, which represent the fused mixtures, which differ in intensity and position from lines appearing in 21, and vice versa, and the entire judgment of the composition of materials, the basis of X-ray diagrams, is based on line position, relative line intensity of the respective scattering patterns.

Q. You stated some time ago, I believe, that the original negatives were clearer than the prints which we are offering in evidence? A. Yes.

Q. Is your opinion as to similarity or dissimilarity based on a study of those original negatives? A. It is based
41 entirely on a study of the original negatives.

Mr. Stowell. The print which the witness has just identified is offered in evidence as Plaintiff Exhibit No. 13.

The Court. It may be admitted.

(The document referred to and identified as Plaintiff Exhibit No. 13 was received in evidence.)

By Mr. Stowell:

Q. I hand you a copy of United States Patent No. 2,059,570 to Fiske and Bryan. Are you familiar with this patent? A. I am.

Q. Is it your opinion, on the basis of tests to which you have testified, that the products obtained by the methods described in the Durgin, et al. application, are identical with the alkaline metal salts of tetraphosphoric acid referred to in this Fiske patent as having been produced by Fleitmann and Henneberg? A. That is correct.

Mr. Stowell. This patent is offered in evidence as Plaintiff Exhibit No. 14.

The Court. It may be admitted.

(The document referred to was marked as Plaintiff Exhibit No. 14 and received in evidence.)

By Mr. Stowell:

Q. Are you familiar with the article from Chemiker Zeitung by Rakuzin and Arseneev, referred to in this patent? A. I am.

42 Q. I hand you a paper marked for identification Plaintiff Exhibit No. 15. Is that a correct translation of the article in the Chemiker Zeitung? A. Yes.

Mr. Stowell. The translation is offered in evidence as Plaintiff Exhibit No. 15.

The Court. It is admitted.

(The document marked for identification as Plaintiff Exhibit No. 15 was received in evidence.)

By Mr. Stowell:

Q. Are you familiar with the prior patents and literature printed in paragraph 12 of the answer of the Commissioner of Patents in this action? A. I am.

Q. Do you find anything in the cited patents or literature of any suggestion or any proposal for the treatment of water by products designated in the literature as alkaline metal tetraphosphate or alkaline metal triphosphate? A. None.

Q. From the basis of the tests to which you have testified, can you state whether or not in your opinion the products obtained by the methods of the Durgin, et al. application are chemically identical with or equivalent to the alkaline metal pyrophosphate, metaphosphate or mixtures thereof, which have been proposed for the treatment of water, for use in the treatment of water by the prior art? A. They are not identical.

43 Q. Are they equivalent? A. No.

Q. On the basis of the tests which you have testified to and your knowledge of the prior art, is it your opinion that the improvement in water-softening properties made by the method of the Durgin, et al. application over substances proposed for the treatment of water in the prior art, would have been obvious or predictable by a skilled chemist at the time of the filing of this application? A. I think not.

Q. On the basis of the tests that you have testified to, and your knowledge of the prior art, is it your opinion that the improvement in water-softening properties, of the products designated in the technical literature as alkaline metal salts of tetraphosphoric acid and sodium triphosphate over the substance proposed for the treatment of water in the prior art, would have been obvious to or predictable by a skilled chemist at the date of the filing of the application? A. That is a long sentence.

Q. That is a rather long, hypothetical question, and the reporter will read it to you.

(Whereupon, the pending question, as above recorded was read by the reporter.)

The Witness. I believe that would not have been.

Mr. Stowell. If your Honor please, the arrival of the certified copies of the file of this application and the parent application and the order of the Patent Office have been delayed, due principally to the fact that half of the Patent
Office is in Richmond. There have been delays, and
44 I think the attorney for the Patent Office will stipu-
late that a certified copy of the file of application Serial No. 733,392 and certified copy of application Serial No. 438,955, as filed, may be placed in the record nunc pro tunc, as of today, when received.

The Court. So stipulated?

Mr. Reynolds. Yes.

Mr. Stowell. That is all.

Cross-Examination

By Mr. Reynolds:

Q. Will you refer, please, to the chart that has been introduced as Exhibit 1 for plaintiff? A. I am familiar with it. Go ahead.

The Court. Page No. 6 of your file.

The Witness. This is it (indicating).

By Mr. Reynolds:

Q. The shaded portion of that chart indicates the range of values which the applicants consider satisfactory, is that right? A. Satisfactory for what purpose?

Q. For water-softening properties. A. That is part of the range which we consider satisfactory.

Q. Well, is it a wider range than you consider satisfactory? A. Well, I believe the allowed claims consider the section from 20-80 to 80-20 as being satisfactory for water-softening purposes.

45 Q. Well, is that the part that is shaded on the chart? A. Oh, yes; the entire shaded area. I beg your pardon.

Q. Now, you testified, did you not, that the yellow portion on the chart indicates the percentages which will produce tetraphosphates; is that right? A. Which will produce materials substantially tetraphosphate.

Q. On what do you base that testimony? A. On the basis of the theoretical calculation of the amount of tetraphosphate which could be present, allowing on either side of the exact theoretical composition for a small excess of either one or the other of the starting materials, but the resulting material having, say, 85 percent or more of the tetraphosphate, in that way qualifying as being substantially sodium tetraphosphate.

Q. And the orange-colored portion on the chart indicates the values that will produce triphosphates, is that right? A. Under the same process of reasoning as was used before.

Q. Well, then, is this a fair statement, then, that the application indicates a certain range in values as satisfactory; that about one-sixth of that range will produce tetraphosphate, one-sixth will produce triphosphate, and the other two-thirds will produce something else? A. Let me hear a restatement of that question, please.

(Whereupon, the pending question, as above recorded, was read by the reporter.)

The Witness. No. That is not a fair statement.

46 By Mr. Reynolds:

Q. Will you please correct it, then? A. Because we have the shaded range representing a range which will produce mostly tetraphosphate, that is, say, 85 percent or more.

Q. Well, do you mean a larger percentage of the range will produce some tetraphosphate; is that the testimony? A. I think that is obvious from the diagram.

Q. Can you indicate what that range would be? A. It is entirely probable that, say, with 10 percent sodium metaphosphate, rather, of 10 percent sodium pyrophosphate with sodium metaphosphate used and prepared under the same conditions as the others would produce some amount of the tetraphosphate.

Q. Then it is your testimony that you would produce some tetraphosphate throughout the whole shaded range; is that true? A. That is possible.

Q. It would be a rather small amount at some parts, wouldn't it? A. In some parts it would be an extremely small amount, that is, the tetraphosphate in those cases might be present as impurities in something else, while in the shaded range the tetraphosphate is the major portion of the material, and the other materials may be present as impurities, we will say.

Q. Now, in the range colored orange, you produce 85 percent of triphosphate, don't you? A. That is on the basis of calculations to the theoretical compositions.

47 Q. So that any tetraphosphate in that range would be a very small amount, would it not? A. Presumably it would be non-existent, except as it might be present as an impurity on the lower side of the theoretical composition for triphosphate.

Q. Well then, there are at least parts of the shaded range that won't produce any material amount of tetraphosphate; is that right? A. Well, now, it happens the example that I gave a moment ago was outside of the shaded range. In the shaded range, that is, between, say, 20 percent sodium pyro-, 80 percent meta-, up to the 60-40, there would be a continuously variable amount of the tetraphosphate formed, you see.

Q. What would you expect at the 20-80 portion of the range? A. Let me see if I can extract something from the previous calculation on that. According to the calculations from the chemical analyses, the 50-50 compositions should contain about 86⅓ percent of the tetraphosphate. The excess, on the basis of the calculations, would be in that case sodium metaphosphate.

Now, going on down the line,—let me see; there is a difference here. No, I wouldn't take a guess without being allowed to calculate.

Q. You couldn't make a guess? A. I wouldn't make a guess without making the calculation. It could be 100 on the basis of impirical formulas, the amount of tetra-
48 phosphate that would be present, or a component in excess.

Q. It would be quite a small amount though, wouldn't it? A. No, I wouldn't say it would be quite a small amount until I could calculate the amount that would be required.

Q. You mean you have no idea what it would be? A. I wouldn't guess at it, but I could calculate it very shortly.

Q. Well, at the upper end of the range, we agreed it would be less than 15 percent, didn't we? A. I believe we made no limit on it.

Q. The tetraphosphate in the orange-colored portion of the chart would necessarily be less than 15 percent? A. Yes, since we have at least 85 percent of triphosphate in that range, on the basis, again, of the calculations from the empirical formulas.

Q. So, at that point on the chart, at least, it would be relatively an insignificant ingredient? A. Presumably it would be.

Q. Vice versa, the triphosphate would be relatively an insignificant ingredient in the yellow portion of the chart, would it not? A. On the basis of the literature, yes.

Q. Well, on the basis of these figures, because didn't you testify that 85 percent of that material was tetraphosphate? A. I said that it was 85 percent tetraphosphate on the basis of calculations from the mechanical composition of the mixture.

49 Mr. Stowell. Might I interrupt to point out that the calculations for various points along this curve appear on this sheet marked Exhibit 7.

By Mr. Reynolds:

Q. Will you refer to Exhibit 7, please, and see if that would help you in giving any more definite testimony. A. Those four columns of figures under "Calculated composition" have been calculated from the observed analyses for sodium oxide and phosphorus pentoxide as indicated in the two columns under "Observed composition".

They have been calculated, assuming that there has been a combination between the sodium oxide and phosphorus pentoxide to form the exact composition $Na_6P_4O_{13}$, and the excess has been calculated as being purely the material left over.

Now, that makes no assumption on my part even of the existence of the tetraphosphate. I simply assume for the purpose of the calculation that theoretical composition as being formed.

Q. Down at the middle of the page on line 17 there is a triphosphate percentage of 99.28 given; is that right? A. That is based there, assuming that triphosphate is formed.

Q. Well, there wouldn't be any material amount of tetraphosphate in that, then, could there? A. Presumably not. I have calculated the excess of that to sodium metaphosphate.

Q. Similarly, in line 25, there is tetraphosphate percentage of 98.92 given. There couldn't be much triphosphate in that, could there? A. Presumably not. 50

Q. So it is fair to say, isn't it, that in the shaded portion of the chart there are some compositions that have no material amount of tetraphosphate in them? A. That is satisfactory.

Q. And there are others that have no material amount of triphosphate in them? A. That, presumably, is right.

Q. Now, it was old, before Durgin, et al. was filed to use phosphate salts of alkali earth metals in treating and softening water, was it not? A. Yes.

Q. Wouldn't that fairly suggest to one skilled in the art that tetraphosphates and triphosphates might be suitable for that purpose? A. Well, mixtures of those corresponding compositions, of course, roughly, had been used, but I believe it was not obvious that the fused product would have such superior properties to the mechanical mixtures.

Q. Well, now, you say "fused mixtures". Of course, these claims are not limited to fused mixtures, are they? A. They are limited to the salts of tetraphosphoric acid as the one set of the claims in issue, but the prior art shows that those salts have been prepared by fusion.

Q. But is that the only way that they could be prepared? A. That is the only way recorded in the literature that I have seen.

Q. You mean, the fusion of these two materials?
51 A. The fusion of any materials which would lead to the composition. We could start with oxide, presumably, and end up with materials of the composition of tetraphosphate or the triphosphate, as we choose, but according to the literature that would result only by carrying it through the fusion.

Q. Now, triphosphate and tetraphosphate salts belong to the class of materials that has been found satisfactory in treating water, don't they? A. I believe prior to this application they had not been found satisfactory.

Q. Well, I mean to say they belong to the class of phosphate salts of alkali earth metals, and that class has been found suitable? A. If you include the end products.

The Court. Of what product?

The Witness. The end product; I mean, the zero percentage of pyrophosphate and metaphosphate or the zero percentage of metaphosphate and pyrophosphate. I will admit that, but not to any of the fused mixtures between those two extremes.

By Mr. Reynolds:

Q. Metaphosphate and pyrophosphate salts of alkali earth metals have been found satisfactory in softening water, have they not? A. Yes.

Q. Don't you think that that would suggest that the salts involved here might also be suitable for that purpose? A. I think there would be no connection there.

Q. You think there is no connection at all? A. I
52 don't think that there is. The previous suggestions
had to do with the use of either of the pure materials
or of mechanical mixtures of those. It had no reference to
any of the other intermediate materials.

Q. Then you think the fact that metaphosphates and pyrophosphates of this material had been found suitable, would not have been even any indication to anyone skilled in the art that tetraphosphates and triphosphates would be suitable? A. I think he would have included them in the same application, if he had.

Q. That would not suggest itself to you. It would strike you as something entirely outside of that, that the tetraphosphates might be tried; is that right? A. It would call for further experimentation; further discovery.

Q. Oh, it would call for experimentation, but wouldn't the idea of experimenting suggest itself to you; that is what I mean. A. I don't get that clear at all.

Q. Wouldn't the fact that metaphosphates and pyrophosphates had been used for softening water, suggest that it might be advisable to try the triphosphates and tetraphosphates? A. I will say I don't know.

Q. You mean you don't know the answer or you don't know that it would be obvious? A. I don't believe it would be obvious.

Q. It would not occur to you from the fact that one might be used that the other might; is that right? A. I believe not.

53 Q. Why would that be? Why would you expect any difference? A. I refuse to answer that question.

Q. Well, do you refuse to answer it? On what ground? A. On the ground that there are claims which have been allowed which, I believe, answer that question entirely from the Patent Office point of view.

Q. Well, you must have some reason if you expect a different result, and I don't see why you can't state the reason. A. You are asking me to pass judgment on something that I am thoroughly familiar with the chemistry of, and what I would consider, beyond going back to my knowledge of the phosphates twelve years ago, what is obvious to me now might not have been obvious to me then, and presumably at that time would not have been obvious to Durgin at all.

Q. Well, of course, I am referring to the ordinary skilled worker in this art. You think it would not suggest itself to him; is that your answer? A. I think that that is the basis of his discovery, that it may have suggested itself to him, requiring experimentation leading to the discovery, that it was new—

Q. Yes, but what I am trying to get at, wouldn't the idea of experimenting with these materials suggest itself to a skilled worker in the art? A. Well, skilled workers are always susceptible to ideas, but not all of those ideas suggested by previous work do lead to an invention, as in the present case they did lead.

54 Q. Well, that is true, but what I want to know is, why it wouldn't suggest itself. These materials are all of the same general class, and you say we find some are suitable, and that doesn't suggest the others are suitable, and I want to know why you think that. A. Well, in the first place, those materials have been known for a long time, dating back, oh, almost one hundred years, yet evidently it had not suggested itself to anyone previous to Durgin, Foster and Booth's work. So, since those men, and many other men, were familiar with chemistry and familiar with the water-softening processes involving the use of sodium metaphosphate and tetrasodium pyrophosphate, I think it is perfectly obvious that it was not obvious to a trained chemist.

Q. Well, the metaphosphates and the pyrophosphates had not been used for water-softening for 100 years, had they? A. No; they have not, but these intermediate compounds have been known that long; the polyphosphates.

Q. Yes, but the thing that would have suggested itself was the use of the metaphosphates and the pyrophosphates. Now, it was not long after that before this application was filed, was it? A. That, I believe, is right.

Q. So that the lapse of time doesn't have much indication there that it was not obvious, does it? A. Don't you think it would have been included in the application for the others, if it had been obvious? It appears to me it would be.

Q. Well, that is the only reason you have, then, the
fact that they didn't think of it, shows it was not
55 obvious? A. Certainly they were trained chemists.

Mr. Reynolds. All right. That is all.

The Court. Any redirect?

Redirect Examination

By Mr. Stowell:

Q. Mr. Reynolds, you stated on cross-examination that the theoretical calculation indicated the materials in the yellow band, the yellow range on Exhibit 1, as being to a very large extent, at least, sodium tetraphosphate and the orange band being to a very large extent, sodium triphosphate.

Did the tests which you have made on the samples within those ranges,—and I refer particularly to water-softening tests and the X-ray diagrams,—confirm your opinion based on the theoretical calculations? A. Yes, it did, because of the close grouping of the two ranges. The compositions, say, in the range shaded yellow showed very similar, almost identical water-softening properties; likewise those in the orange range showed very closely identical water-softening properties; hence the shadings do have significance in that they separate the two compositions into two different groups so far as water-softening properties are concerned, also so far as X-ray diagrams are concerned.

Mr. Stowell. That is all, your Honor.

Mr. Reynolds. That is all.

The Court. Call your next witness.

Mr. Stowell. That is our case, your Honor.

The Court. Any evidence by the Commissioner?

56 Mr. Reynolds. I would just like to offer the exhibit that I handed your Honor at the start of the trial.

The Court. Any objection?

Mr. Stowell. No, sir.

The Court. It may be admitted.

(The document referred to was admitted in evidence as Defendant's Exhibit No. 1.)

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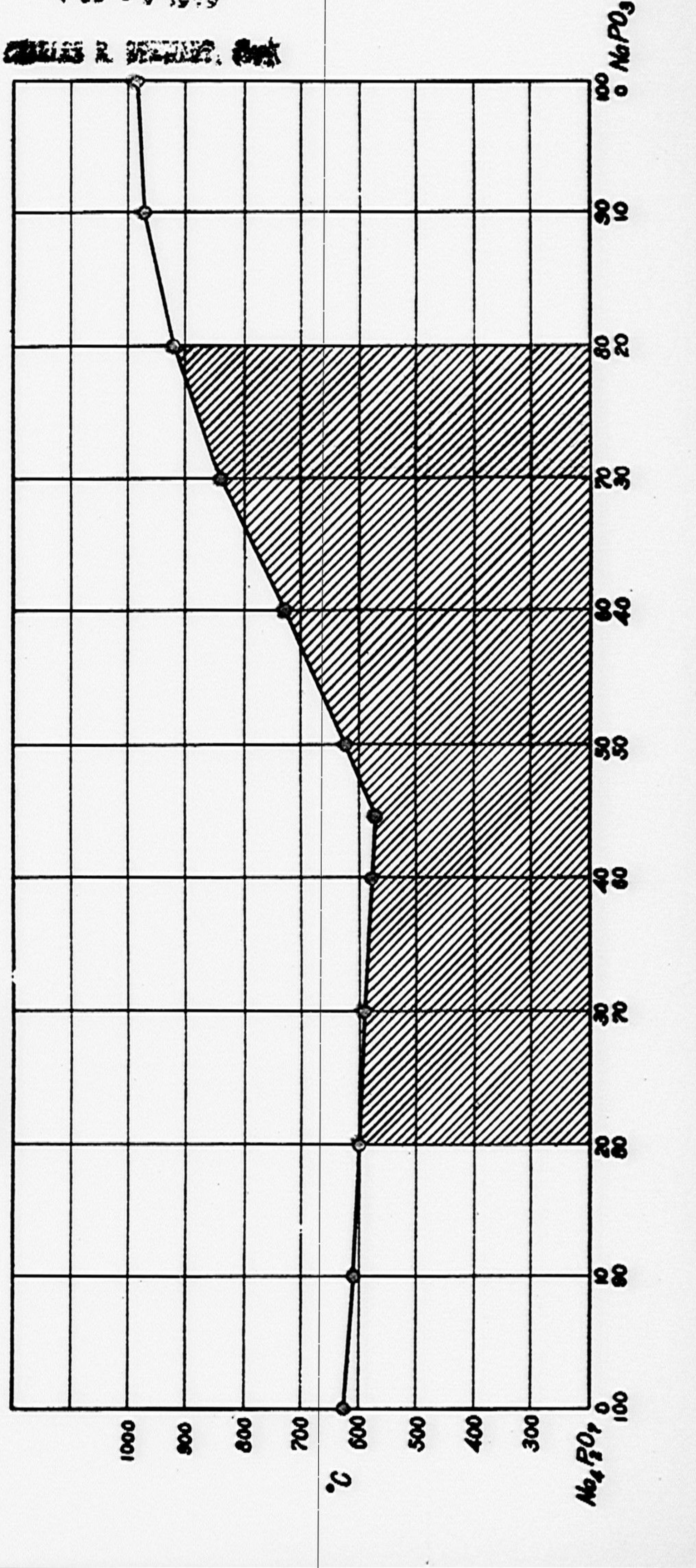
APPELLANT'S EXHIBIT NO. 1

FILED
FEB 10 1943
CHARLES E. STEWART, Clerk

C.A. No. 13,279



Civil Action - 13279

MONSANTO CHEMICAL CO.,
et al
vs.
CONWAY P. COE

APPELLANT'S EXHIBIT NO. 2.

69 *Translation*

From Dammers Handbuch der Anorgan. Chemies 1894,
Bd. 2, I pages 124 and 125.

"In the same manner than 2 mol. H_3PO_4, upon the loss of 1 mol. H_2O combine to form pyrophosphoric acid; it is possible for m Mol. H_2PO_4 to combine with the loss of (m-l) Mol. H_2O. Up to the present time only two condensed acids are known.

Tetraphosphoric acid, $H_6P_4O_{13}$. The Na salt, according to Fleitmann and Henneberg (A *65,* 30) is formed by melting together $NaPO_3$ and $Na_4P_2O_7$ or by melting together $NaPO_3$ and Na_3PO_4, it is also formed from sodium hexametaphosphate together with pyrophosphate or orthophosphate according to:

$$Na_6P_6O_{18} + 3Na_4P_2O_7 = 3Na_6P_4O_{13} \text{ and}$$
$$Na_6P_6O_{18} + 2Na_3PO_4 = 2Na_6P_4O_{13}.$$

From the cooled melt, hot H_2O dissolves out the crystallizable sale. Upon extending heating of the solution it passes into the orthophosphate. By double decomposition one obtains from the Na salt, the salts of other metals. On this, by Fleitmann and Henneberg so-called sesquiphosphate, compare also Gerhardt, (C. v. des trav. chim. *1849,* 12) and Krant and Uelsmann (A. *118,* 99)

Decaphosphoric acid $H_{12}P_{10}O_{31}$. The Na salt is obtained by melting together $4Na_8P_6O_{18}$ with $3Na_4P_2O_7$ (Fleitmann and Henneberg)."

APPELLANT'S EXHIBIT NO. 3.

70 *Translation*

Parravano and Calcagni, "Die Polyphosphate"
Zeitschrift für Anorganische Chemie, Vol. 65, 1910

Page 3, lines 17-29

"The polyphosphates may be regarded as products resulting from the combination of pyrophosphate and metaphosphate; they form the following sodium salts:

$$Na_4P_2O_7 + NaPO_3 = Na_5P_3O_{10},$$
$$Na_4P_2O_7 + 2NaPO_3 = Na_6P_4O_{13},$$
$$Na_4P_2O_7 + 8NaPO_3 = Na_{12}P_{10}O_{31}.$$

"The various types of polyphosphates are obtained in fact by fusing together pyro- and metaphosphate in various proportions. The nature and the number of products which are formed by the combination of pyrophosphate with metaphosphates can therefore be determined by studying the diagram obtained for these pairs of salts by thermo analyses."[1]

APPELLANT'S EXHIBIT NO. 4-A AND B.

Ephraim, Inorganic Chemistry (1926), pages 622 and 623.

71 Pyrophosphoric Acid is also crystallised with difficulty and is mostly obtained as a glass. Neverthless, turbid sugar-like, crystalline forms have occasionally been observed, and it was then noted that the acid did not melt below 61°—higher than the the ortho-acid. After melting it solidifies again in the crystalline state, but with difficulty.

The salts of these acids are better defined than the free acids. The pyrophosphates are obtained only in two stages of neutralisation—as quaternary and secondary salts, $M_4P_2O_7$ and $M_2H_2P_2O_7$, although the acid contains four hydrogen atoms. Of these, the alkali and thallium salts are soluble in water, the partially deliquescent potassium salt being the most soluble. The quaternary alkali salts are slightly hydrolysed. The quaternary salts of other metals, most of which are described as being powdery, are all insoluble in water, but the secondary salts are soluble and crystalline. The insoluble pyrophosphates dissolve in an excess of alkali pyrophosphate with the formation of complex compounds, which are comparable to the complex thiosulphates (p. 459). The formulae

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[1] Tammann, Zeitschrift für Anorganische Chemie 37 (1903), 303; 45 (1905), 24; 47 (1905), 298. Plato, Zeitschrift der physikalischen Chemie 55 (1906), 727; 58 (1907), 350.

$$Na_2CuP_2O_7, \text{ aq.}, \quad Na_4Mn_2(P_2O_7)_2, \text{ aq.}, \quad K_8Mn_2(P_2O_7)_3, \text{ aq.}$$

may be quoted as examples.

The tri- and tetraphosphoric acids (p. 619), $H_5P_3O_{10}$ and $H_6P_4O_{13}$, are not known in the free state, but their sodium salts are obtained by fusing together suitable quantities of sodium pyro- and metaphosphates. They are probably not to be regarded as double salts of pyro- and metaphosphates, but rather as corresponding to special stages in dehydration, since they cannot be obtained by evaporating mixed aqueous solutions of pyro- and metaphosphates. They decompose in solution, particularly on heating and in presence of acids or alkalis, giving pyro- and meta-salts. In general, their properties lie between those of the pyro- and metaphosphates, but the tetraphosphate is distinct from the metaphosphate in the solubility of its silver salt in an excess of the sodium salt. The triphosphates also show solubilities which are different from those of the components; e.g. chromium sulphate in a solution of triphosphate gives a precipitate much more easily than in one which contains a mixture of pyro- and metaphosphates in the proportions required by the triphosphate formula. The double compounds of the formula $MNa_3P_3O_{10}$ (usually $+ 12H_2O$) are characteristic of the triphosphates; M is a bivalent metal such as Cu, Fe, Zn, Mn, Ni Co, and these salts crystallise from fairly concentrated solutions of the sodium salt on the addition of heavy metal salts.

Metaphosphoric acid, HPO_3, and its salts possess the most complicated properties of all the acids of phosphorus, because, on the one hand, they have a strong tendency to polymerize, when varied products of high molecular weight can be formed, while on the other hand, these products show isomerism through the different arrangement of
72 the individual molecules, so that varying constitutions may appear with the same molecular complexity. The relations of the metaphosphates are still so confused, in spite of numerous investigations, that the practice of giving definite formulae for the products must be given up for the present.

The metaphosphates are formed by heating together the calculated quantities of phosphoric acid and metallic oxides. The properties of the metaphosphate formed differ according to the nature of the oxide employed; they also vary with the temperature used. Further, metaphosphates are formed on heating the primary ortho- or the acid pyrophosphates, with the elimination of water:

$$MH_2PO_4 = MPO_3 + H_2O, \qquad M_2H_2P_2O_7 = 2MPO_3 + H_2O.$$

Here also the condition of the product formed is entirely dependent on the method of heating, and by changing the rate of cooling of the melt various highly polymerised products are produced. Even ordinary "microcosmic salt," $NaNH_4PO_4$, does not give a homogeneous metaphosphate on heating. If the ammonia and water are driven off a melt is obtained, which breaks down into two different salts when water is poured on to it. One is easily soluble in water and the other completely insoluble. If this is heated further, it passes into a glassy form, which is likewise a mixture of several modifications. Fleitmann and Henneberg[1] attempted to estimate the molecular size from the formulae of the double salts obtained. Thus a series of dimetaphosphates of the form $KNa(PO_3)_2$ could be isolated. They were later shown to be tetrametaphosphates, $M_4(PO_3)_4$, since their conductivities, measured at the dilutions 1/32 and 1/1024, differed by about 40 reciprocal ohms; for according to the Ostwald-Walden Rule the basicity of an acid is equal to the conductivity changes between these dilutions divided by 10. Thus, here $40 \div 10 = 4$. At 25° the conductivity is

Dilution	Na salt	K salt	NH_4 salt	Li salt
n/32	85.6	102.8	100.2	81.7
n/1024	126.2	146.7	142.9	123.3
Difference	40.6	43.9	42.7	41.6

The double salts such as $NaCa(PO_3)_3$ have been similarly regarded as trimetaphosphates with some degree of probability, but the constitution of still more highly polymerised metaphosphates has not yet been decided. Still, it appears that polymerization series with 2, 3, 4, 5, 6, 8, 10, 14 and other members have been identified. Several were first obtained in the form of heavy metal salts; the heavy metal may then be precipitated by sulphuretted hydrogen, and the alkali salt formed from the product by addition of alkali hydroxide. Others again can only

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[1] *Ann.*, 1848, 65, 304.

APPELLANT'S EXHIBIT NO. 5-A AND B.

Mellor, Inorganic and Theoretical Chemistry, Vol. 8, 1928, pages 990 and 991.

73 There is some doubt if some of the polymetaphosphates are really chemical individuals, and if some of the individual metaphosphates have been inserted in the right class. Decisive evidence is usually wanting, for, in spite of the many researches which have been made on the metaphosphates, their chemistry is by no means in a satisfactory condition. As F. Warschauer said in 1903, the metaphosphates form one of the most confused chapters of inorganic chemistry.

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[1] E. Cornee, Contribution à l'étude physicóchimique de la neutralization, Paris, 103, 1912; Ann. Chim. Phys., (8), 29. 490, 1913; (8), 30. 63, 1913; T. Fleitmann, Liebig's Ann., 72. 228, 1849; T. Fleitmann and W. Henneberg, ib., 65. 304, 1848; W. Gregory, ib., 54. 94, 1844; R. Maddrell, Phil. Mag., (3), 30. 322, 1847; Mém. Chem. Soc., 3. 273, 1847; T. Graham, Phil. Trans., 123. 253, 1833; S. Arrhenius, Zeit. phys. Chem., 1. 631, 1887; G. Tammann, ib., 6. 122, 1890; Journ. prakt. Chem., (2), 45. 417, 1892; C. G. Lindbom, Lund's Univ. Arsskr., 10, 1874; Ber., 8. 122, 1875; L. Jawein and A. Thillot, ib., 22. 654, 1889; A. Glatzel, Ueber Dimetaphosphorsäure und Tetrametaphosphorsäure Salze, Würzburg, 1880; P. Pascal, Bull. Soc. Chim., (4), 33. 1611, 1923; Compt. Rend., 177. 1298, 1923; 178. 211, 1924; 179.

966, 1924; 180. 664, 1924; G. von Knorre, Zeit. angew. Chem., 5. 639, 1892; Zeit. anorg. Chem., 24. 369, 1900; H. Lüdert, ib., 5. 15, 1894; A. Wiesler, ib., 28. 177, 1901; Beiträge zur Kenntnis der Metaphosphate, Berlin, 1901; J. Müller, Beiträge zur Kenntnis der Metaphosphate, Berlin, 1906; F. Warschauer, Beiträge zur Kenntnis der Metaphosphate, Leipzig, 1903; ib., 36. 137, 1903; M. Berthelot and G. André, Compt. Rend., 124. 265, 1897; Ann. Chim. Phys., (7), 11. 204, 1897; S. Tanatar, Journ. Russ. Phys. Chem. Soc., 30. 99, 1898; G. Rose, Sitzber, Acad. Berlin, 129, 450, 1867; A. Holt and J. E. Myers, Journ. Chem. Soc., 99. 394, 1911; A. Jamieson, Liebig's Ann., 59. 350, 1846.

§ 28. Polyphosphoric Acids

Pyrophosphoric acid can be considered as a member of a series of polyphosphoric acids. They can be derived from ordinary phosphoric acid by the abstraction of water, thus:

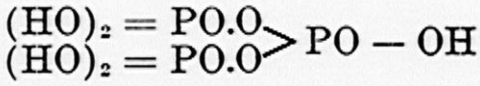
Pyrophosphoric acid, $H_4P_2O_7$	$2H_3PO_4$ less H_2O
Triphosphoric acid, $H_5P_3O_{10}$	$3H_3PO_4$ less $2H_2O$
Tetraphosphoric acid, $H_6P_4O_{13}$	$4H_3PO_4$ less $3H_2O$

The general formula is $mH_3PO_4-(m-1)H_2O$, or $H_nP_{n-2}O_4$ $+(n-3)_3$. For example:

Orthophosphoric acid ($m = 1$)	H_3PO_4
Di- or pyro-phosphoric acid ($m = 2$)	$H_4P_2O_7$
Triphosphoric acid ($m = 3$)	$H_5P_3O_{10}$
Tetraphosphoric acid ($m = 4$)	$H_6P_1O_{13}$

Salts of some of these acids were made by T. Fleitmann and W. Henneberg,[1] P. Glühmann, F. Schwarz, and M. Stange, by heating metaphosphates with
74 pyro- or ortho-phosphates. On cooling a fused mixture of anhydrous sodium pyrophosphate (100 parts) with sodium metaphosphate (50 parts) which has been kept at a bright red-heat for about half an hour, a crystalline

mass of sodium triphosphate, $Na_5P_3O_{10}$, is obtained: $Na_4P_2O_7+NaPO_3=Na_5P_3O_{10}$. The conc. aq. soln. furnishes crystals corresponding with $Na_5P_3O_{10}.8H_2O$—a result not obtained by simply evaporating a soln. of the two salts in water, and which has been used against the argument that the alleged triphosphate is a double salt of sodium pyro- and meta-phosphates. The aq. soln. when boiled decomposes into a mixture of the two components. Various double salts have been prepared of the type $M''Na_3P_3O_{10}$, by treatment with cobalt, zinc, and other salts. Zinc and manganese salts of the type $M''_2NaP_3O_{10}$ have been made. M. Stange found that when titrated with 1:10 soln. of ferrous ammonium sulphate, lead nitrate, manganese sulphate, cadmium sulphate, or barium chloride rather more liquid is required to produce a precipitate with a soln. of triphosphate than with an eq. mixture of meta- and pyro-phosphates; rather less with a soln. of chrome-alum, and just the same with silver nitrate. F. Schwarz claims to have made the free acid—triphosphoric acid, $H_5P_3O_{10}$—by treating an aq. soln. of the copper salt with hydrogen sulphide. The aq. soln. of the acid is soon transformed into pyrophosphoric acid, $2H_5P_3O_{10}+H_2O\longrightarrow 3H_4P_2O_7$, and albumen is not coagulated; if, however, the sodium salt is treated with a few drops of acetic acid, the albumen is coagulated. F. Schwarz represented the constitution



$$\begin{matrix}(HO)_2=PO.O \\ (HO)_2=PO.O\end{matrix}\!\!>PO-OH$$

in agreement with the phneyl triphosphate obtained by M. Riegel.

T. Fleitmann and W. Henneberg also prepared sodium tetraphosphate, $Na_6P_4O_{13}$—representing tetraphosphoric acid, $H_6P_4O_{13}$—by melting together a mixture of eq. amounts of sodium hexametaphosphate, $Na_6P_6O_{18}$, and sodium pyrophosphate: $Na_6P_6O_{18}+3Na_4P_2O_7=3Na_6P_4O_{13}$; or with sodium orthophosphate: $Na_6P_6O_{18}+2Na_3PO_4=2Na_6P_4O_{13}$. Sodium tetraphosphate can be crystallized from its soln. in hot water, although it is slowly transformed into the orthophosphate in warm aq. soln. An acid salt has not been made, but silver and magnesium salts of a similar composition have been made by double decomposition of the sodium salt with salts of the respective elements. If sodium salts were those of a hexametaphosphate, they should give no precipitate with magnesium salts, and with silver salts a precipitate soluble in an excess of the sodium salt. C. F. Gerhardt thought the salt crystallizing with 18 mols. of water of crystallization to be an acid salt of pyrophosphoric acid, but K. Kraut and H. Uelsmann found that this is not likely to be the case because all the water is lost in a desiccator over sulphuric acid. M. A. Rakusin and A. A. Arsenéeff found that after the violent reaction resulting from the addition of phosphoric oxide to water and formation of orthophosphoric acid has subsided, further quantities are gradually added until the amount reaches about 520 per cent. of the water present. After keeping for five days, crystals of tetraphosphoric acid, $H_6P_4O_{13}$, separate from the syrupy liquid. This acid has previously only been prepared in the form of its salts. The acid melts at 34°, and has a sq. gr. of 1.8886 at 15°.

T. Fleitmann and W. Henneberg also prepared sodium decaphosphate, $Na_{12}P_{10}O_{31}$—representing decaphosphoric acid, $H_{12}P_{10}O_{31}$—by fusing together eq. quantities of sodium hexametaphosphate and sodium pyrophosphate: $4Na_6P_6O_{18} + 3Na_4P_2O_7 = 3Na_{12}P_{10}O_{31}$.

A. V. Kroll[2] reported a series of salts which he called ultra-phosphates, but the following is not his view of their nature. Assuming the ultra-phosphates are chemical individuals, they can be derived from the orthohexaphosphoric acid, $H_{20}P_6O_{25}$, or $(HO)_4P.O.P(OH)_3.O.P(OH)_3.O.P(OH)_3.O.P(OH)_3.O.P(OH)_4$, by the loss of five mols. of water so as to form penterohexaphosphoric acid, $H_{10}P_6O_{20}$.

APPELLANT'S EXHIBIT NO. 6

C.A. No. 13,279

①
$$Na_2CO_3 + 2H_3PO_4 \longrightarrow 2NaH_2PO_4 + CO_2 + H_2O$$
(Sodium Carbonate) (Phosphoric Acid) (Mono Sodium Phosphate)

②
$$Na_2CO_3 + H_3PO_4 \longrightarrow Na_2HPO_4 + CO_2 + H_2O$$
(Sodium Carbonate) (Phosphoric Acid) (Di Sodium Phosphate)

③
$$NaH_2PO_4 \xrightarrow{Heat} NaPO_3 + H_2O$$
(Mono Sodium Phosphate) (Sodium Metaphosphate)

④
$$2Na_2HPO_4 \xrightarrow{Heat} Na_4P_2O_7 + H_2O$$
(Di Sodium Phosphate) (Sodium Pyrophosphate)

⑤
$$Na_4P_2O_7 + NaPO_3 \xrightarrow{Fusion} Na_5P_3O_{10}$$
(Sodium Pyrophosphate) (Sodium Metaphosphate) (Sodium Triphosphate)

⑥
$$Na_4P_2O_7 + 2NaPO_3 \xrightarrow{Fusion} Na_6P_4O_{13}$$
(Sodium Pyrophosphate) (Sodium Metaphosphate) (Sodium Tetraphosphate)

⑦
$$5Na_2CO_3 + 6H_3PO_4 \longrightarrow 2NaH_2PO_4 + 4Na_2HPO_4 + 5CO_2 + 5H_2O \xrightarrow{Heat}$$
(Sodium Carbonate) (Phosphoric Acid) (Mono Sodium Phosphate) (Di Sodium Phosphate)
$$\longrightarrow 2NaPO_3 + 2Na_4P_2O_7 + 4H_2O \xrightarrow{Fusion} 2Na_5P_3O_{10}$$
(Sodium Metaphosphate) (Sodium Pyrophosphate) (Sodium Triphosphate)

⑧
$$3Na_2CO_3 + 4H_3PO_4 \longrightarrow 2NaH_2PO_4 + 2Na_2HPO_4 + 3CO_2 + 3H_2O \xrightarrow{Heat}$$
(Sodium Carbonate) (Phosphoric Acid) (Mono Sodium Phosphate) (Di Sodium Phosphate)
$$\longrightarrow 2NaPO_3 + Na_4P_2O_7 + 2H_2O \xrightarrow{Fusion} Na_6P_4O_{13}$$
(Sodium Metaphosphate) (Sodium Pyrophosphate) (Sodium Tetraphosphate)

FILED
FEB 10 1943
CHARLES H. STEWART, Clerk

C.A. No. 13,279

APPELLANT'S EXHIBIT NO. 7

✓ POLYPHOSPHATE TEST SAMPLES

Book Page No.		Starting Materials	Treatment	Nominal Composition		Theoretical Composition		Observed Composition		Calculated Composition				Melting Point °C	pH 1% Solution	Water Softening Test
				$Na_4P_2O_7$	$NaPO_3$	Na_2O	P_2O_5	Na_2O	P_2O_5	$Na_6P_4O_{13}$	$Na_5P_3O_{10}$	$Na_4P_2O_7$	$NaPO_3$			
599	01	$NaPO_3 + Na_4P_2O_7$	fused, chilled from 950°C	50	50	38.51	61.49	38.30	61.70	86.33	—	—	13.67	635	8.59	1500
	02	" "	" " " "	56.6	43.4	39.58	60.42	39.15	60.55	96.62	—	—	3.38	735	8.91	1500
	03	" "	" " " "	60	40	40.13	59.87	40.05	60.15	94.29	—	5.71	—	780	8.78	1990
	04	" "	" " " "	70	30	41.75	58.25	41.60	58.40	—	95.52	—	4.48	850	9.06	2560
	05	" "	" " " "	72.3	27.7	42.12	57.88	42.10	58.00	—	99.57	—	0.43	860	9.26	3470
	06	" "	" " " "	80	20	43.38	56.62	43.30	56.65	—	71.51	28.49	—	910	9.41	4010
599	07	fused $NaPO_3 + Na_4P_2O_7$	fused, chilled from 950°C	50	50	38.51	61.49	38.20	61.80	86.58	—	—	13.42	640	8.54	1630
	08	" " "	" " " "	56.6	43.4	39.58	60.42	39.35	60.50	98.11	—	—	1.89	740	8.90	1900
	09	" " "	" " " "	60	40	40.13	59.87	40.15	59.85	86.06	—	13.94	—	770	8.95	1920
	10	" " "	" " " "	70	30	41.75	58.25	41.70	58.25	—	97.94	—	2.06	850	9.36	2980
	11	" " "	" " " "	72.3	27.7	42.12	57.88	42.10	57.90	—	99.83	—	0.17	865	9.26	3160
	12	" " "	" " " "	80	20	43.38	56.62	43.15	56.65	—	74.91	25.09	—	920	9.45	3840
599	13	$NaH_2PO_4 + Na_2HPO_4$	fused, chilled from 950°C	50	50	38.51	61.49	38.70	61.30	87.70	—	—	12.30	635	8.60	1920
	14	" "	" " " "	56.6	43.4	39.58	60.42	39.60	60.20	98.39	—	—	1.61	735	8.78	1920
	15	" "	" " " "	60	40	40.13	59.87	40.10	59.65	90.67	—	9.08	—	775	8.83	1920
	16	" "	" " " "	70	30	41.75	58.25	41.85	58.00	—	98.19	—	1.81	860	9.22	2980
	17	" "	" " " "	72.3	27.7	42.12	57.88	42.05	58.00	—	99.23	—	0.77	865	9.29	2980
	18	" "	" " " "	80	20	43.38	56.62	43.15	56.60	74.42	—	25.33	—	915	9.44	4010
599	19	fused $NaPO_3 + Na_4P_2O_7$	mechanical mixture	50	50	38.51	61.49	38.45	61.30	—	—	50.33	49.37	—	9.07	2630
	20	" " "	" "	56.6	43.4	39.58	60.42	39.70	60.25	—	—	55.81	44.19	—	9.15	2980
	21	" " "	" "	60	40	40.13	59.87	40.10	60.00	—	—	59.56	40.44	—	9.20	3330
	22	" " "	" "	70	30	41.75	58.25	41.77	58.32	—	—	70.11	29.81	—	9.43	6200
	23	" " "	" "	72.3	27.7	42.12	57.88	42.15	58.00	—	—	72.16	27.79	—	9.67	5980
	24	" " "	" "	80	20	43.38	56.62	43.35	56.65	—	—	79.84	20.16	—	9.90	5620
599	25	$NaPO_3 + Na_4P_2O_7$	fused, chilled from 750°C	56.6	43.4	39.58	60.42	39.45	60.45	99.02	—	—	0.98	730	8.91	1540
	26	$H_3PO_4 + Na_2CO_3$	" " " 950°C	80	20	43.38	56.62	43.10	57.45	—	83.33	16.67	—	905	9.32	3160
	27	Quadriphos from Am. Cyanamide Co.		—	—	—	—	37.65	60.05	88.89	—	—	11.11	620	7.55	1350
	28	Tripoly, Victor, from Calgon		—	—	—	—	41.85	57.10	—	92.77	—	7.23	895	9.26	3500
	A	fused $NaPO_3$, chilled from 750°C		—	100	30.40	69.60	—	—	—	—	—	—	625	~acid	11600
	B	$Na_4P_2O_7$, C.P. anhydrous		100	—	46.62	53.38	—	—	—	—	—	—	985	basis	7720

A and B were used in preparing samples
1–25, incl., where indicated

● After adjusting to pH 9 with NaOH

APPELLANT'S EXHIBIT NO. 8

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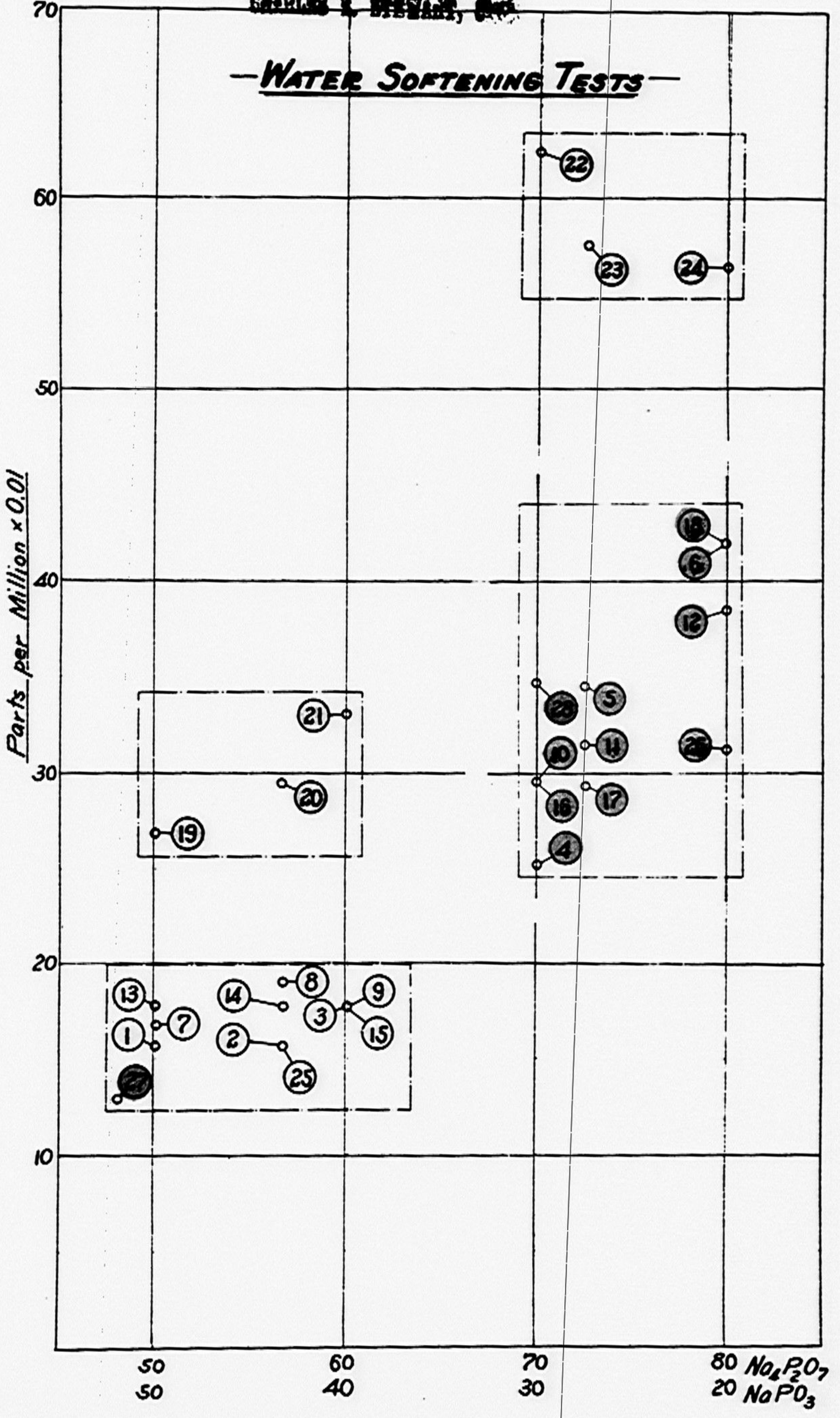
FEB 10 1943
CHARLES E. STEWART, Clerk

C.A. No. 13,279



APPELLANT'S EXHIBIT NO. 9

C.A. No. 13,279

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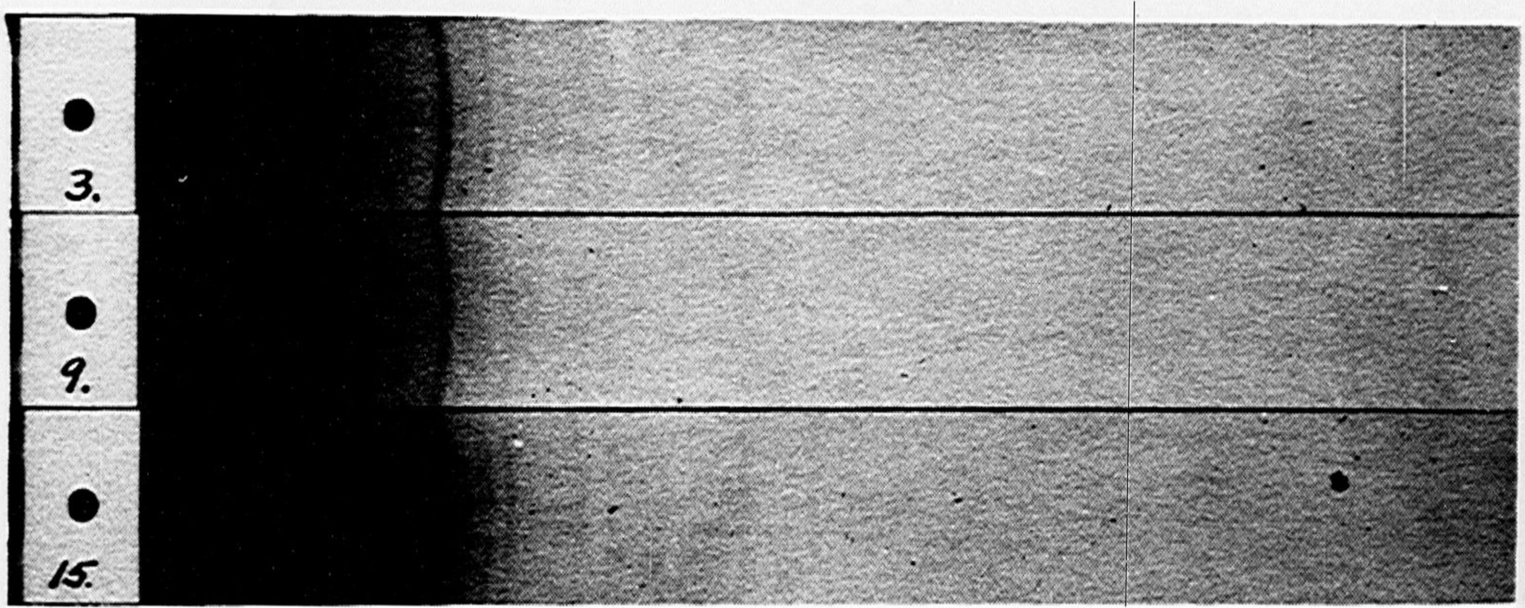

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C.A. No. 13,279

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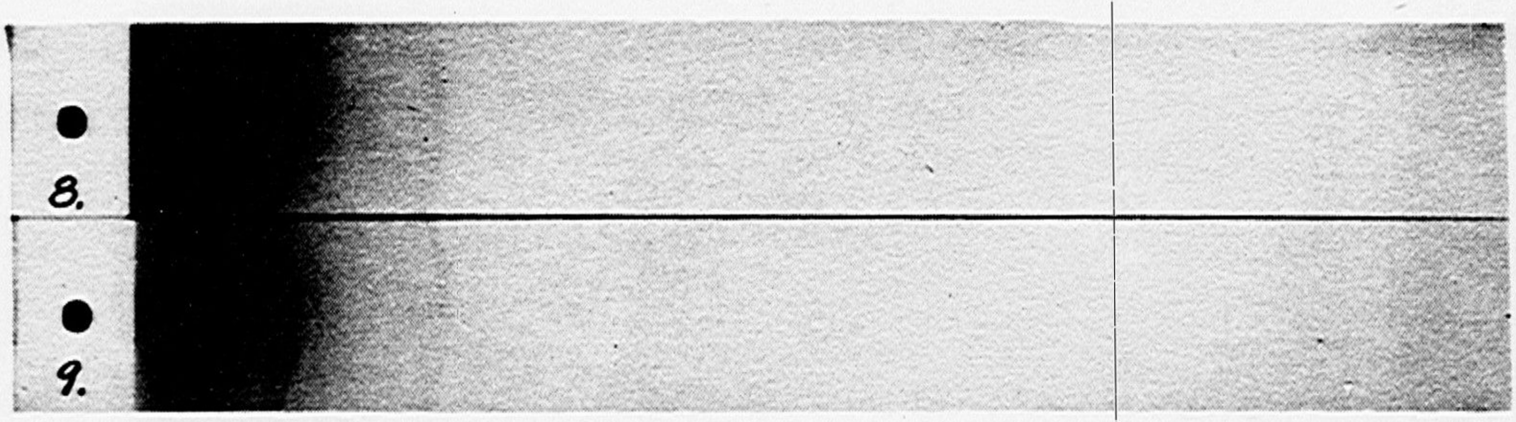

APPELLANT'S EXHIBIT NO. 11

C.A. No. 13,279

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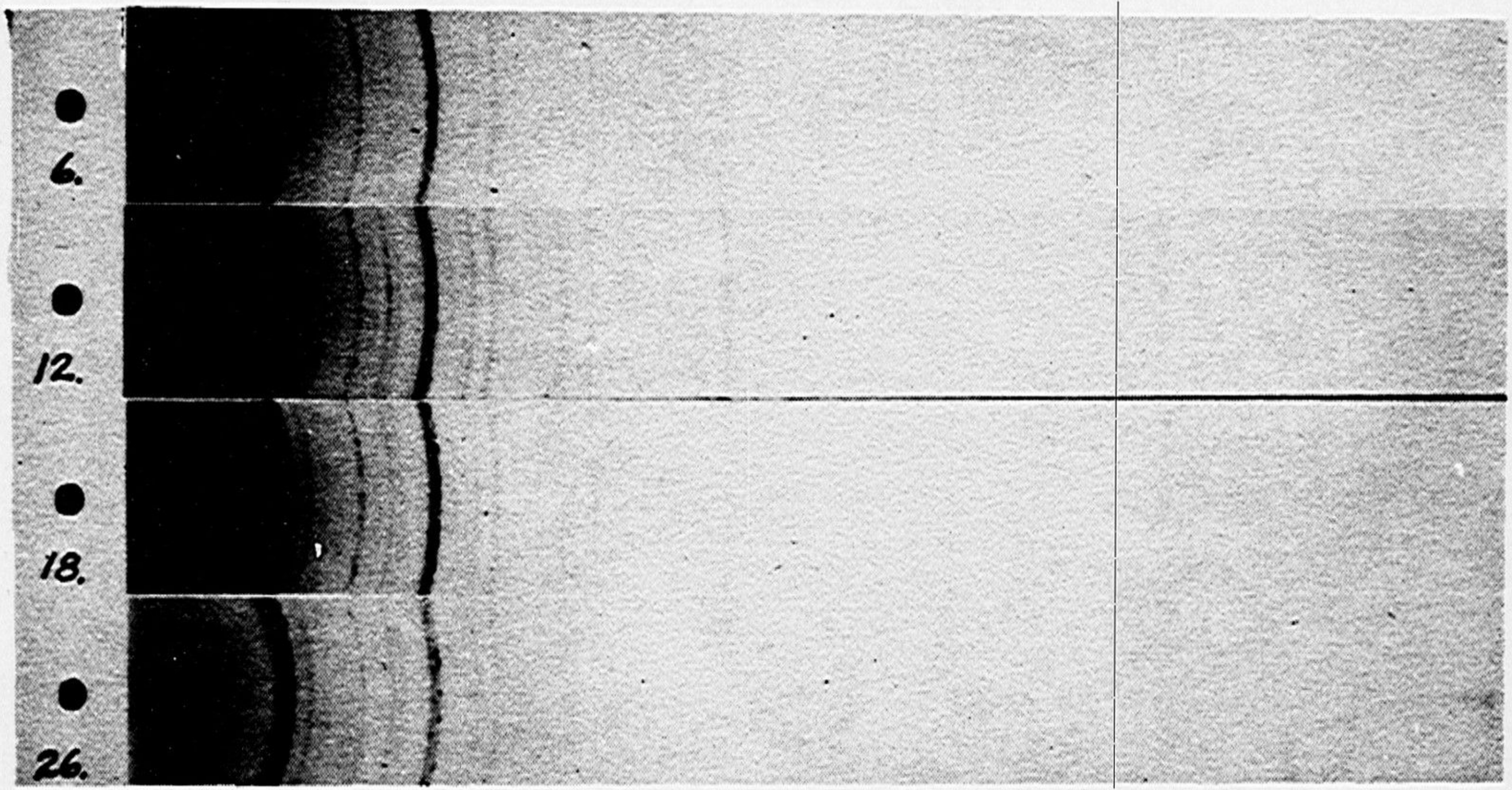
[redacted] STEWART, Clerk



APPELLANT'S EXHIBIT NO. 12

C.A. No. 13,279

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FEB 16 1943
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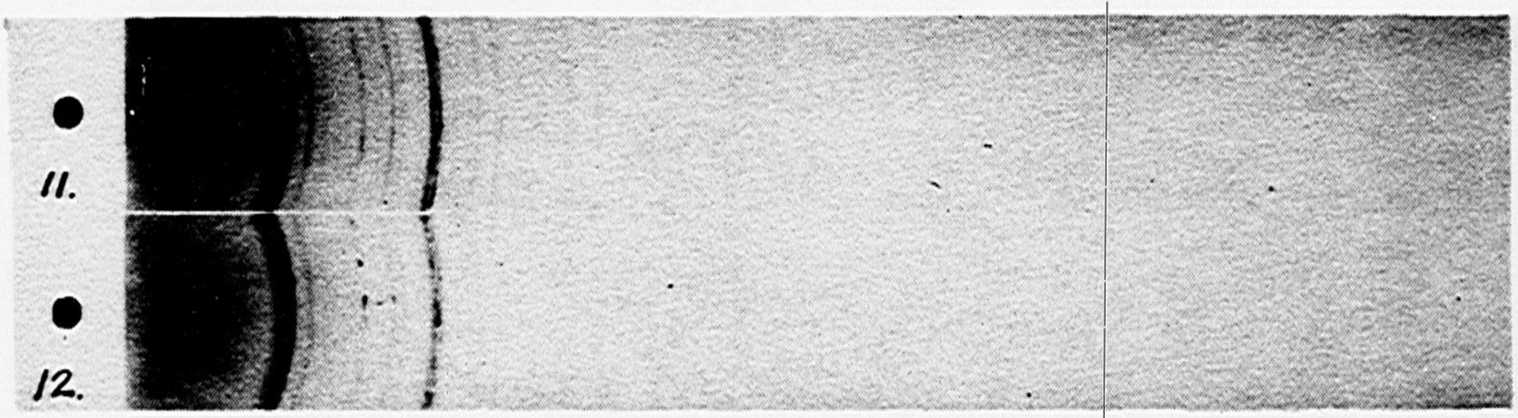


APPELLANT'S EXHIBIT NO. 13

C.A. No. 13,279

FILED

FEB 10 1943

CHARLES R. STEWART, Clerk

APPELLANT'S EXHIBIT NO. 14.

Patented Nov. 3, 1936 **2,059,570**

UNITED STATES PATENT OFFICE

2,059,570

PROCESS FOR SOFTENING WATER AND DISSOLVING CALCIUM SALTS

Augustus H. Fiske, Warren, and Charles S. Bryan, Providence, R. I., assignors to Rumford Chemical Works, Rumford, R. I.

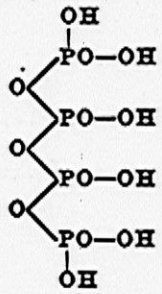
No Drawing. Application December 7, 1934, Serial No. 756,459

6 Claims. (Cl. 210—23)

Our invention relates paraticularly to a method for softening water, such, for instance, as water which is hard by reason of the presence of calcium or other salts, and for dissolving these salts in such a manner as to decrease or eliminate the hardness of the water, and particularly by the use of soluble tetraphosphates.

The object of my invention is to provide a more advantageous method for the softening of water so as to eliminate the hardness thereof, by dissolving the said salts with the aid of soluble tetraphosphates, that is to say, the tetraphosphates of the alkali metals. The tetraphosphates to which I refer are the salts of the tetraphosphoric acid discovered by Fleitmann and Henneberg in 1848 and having the following constitution, as set forth by Roscoe and Schorlemmer in their Treatise on Chemistry, vol. 1, Macmillan & Co., Ltd., 1905, page 656,—

Tetraphosphoric acid



This is not to be confused with the so-called "tetraphosphate" fertilizer discovered by Stoppani in 1911, and which was made by heating the carbonates of sodium, magnesium, calcium and sulphate of sodium with natural mineral phosphates to a temperature of about 600° C., a process developed to make the mineral phosphate merely available as a plant fool. The product made by Stoppani was doubtless called "tetraphosphate" because of the fact that four ingredients were used in its preparation, in addition to the mineral phosphate present and the name applied thereto was evidently merely a trade term, his product being understood to be a double orthophosphate of calcium and sodium. The tetraphosphates produced by Fleitmann and Henneberg have the general formula $R_6P_4O_{13}$, where R signifies the base, and were made up then by fusing together pyrophosphates and metaphosphates, also orthophosphates and metaphosphates. Also, sodium tetraphosphate is referred to in the British patent to Patten, No. 8197 of 1901, as being made by a reaction between sodium bicarbonate and acid sodium pyrophosphate. Also, according to Chem. Ztg., Rakuzin and Arseneev, 1923, pages 47, 195, prepared tetraphosphoric acid, $H_6P_4O_{13}$, and the salts forming the subject matter of the present application, are the salts of the acid there referred to. The water softening may be carried out according to our method by using the true alkali tetraphosphates made in accordance with any of the above procedures, but preferably it is carried out by utilizing an alkali tetraphosphate, and particularly sodium tetraphosphate as made in accordance with the process set forth in our co-pending application upon Process of making tetraphosphates and product thereof, Ser. No. 756,457, filed December 7, 1934, which has matured into Patent No. 2,031,827, Feb. 25, 1936.

While our invention is capable of being carried out in many different ways, for the purpose of illustration we have described hereinafter only certain embodiments of our invention.

The water softener made in accordance with our invention may be applied in such a manner as to soften the water containing soluble calcium salts with or without the presence of other soluble salts, as, for instance, magnesium salts, for the following uses:

As a water softener by keeping the alkali earth bases in a soluble condition.

In laundries to save soap by combining with the alkali earth bases in the washing water.

In deliming leather as in the tanning industry.

In dissolving the lime compounds which may occur in soiled textiles.

To prevent deposits of alkali earth salts forming in hot water systems.

To prevent deposits of alkali earth compounds in steam boilers and their feed lines.

To prevent deposits of alkali earth compounds in automobile water cooling systems.

To prevent the formation of alkali earth bases as precipitates in the water to be frozen in artificial ice machines.

To prevent the formation of alkali earth precipitates on the outside of cans from the cooling water of the canning industry.

To prevent streaky dyeing in textiles by keeping any alkali earth compounds in a condition of solubility.

Preventing the formation of soap spots on the cloth in dyeing.

To clean cement or brick walls from lime deposits.

As a softener for water in washing living animals or in baths for human beings.

For cleaning or washing dishes.

For softening water in which anything may be washed and thus saving soap.

Washing rayon, for instance.

Scouring wool.

Kier boiling in bleacheries.

Boiling off silk.

Causing increased penetration of dye in textiles by cleaning off traces of alkali earth compounds.

As so applied it is found that the water softening, by adding an alkali metal tetraphosphate, is much more effective than previous methods of water softening. For example, to soften the water used in laundries for the washing of fabrics, or in preventing the deposit of alkali earth compounds in steam boilers and other feed lines, with water containing soluble lime salts with or without the presence of magnesium salts, etc., we add to 1000 gallons of water containing, for instance, 48 parts by weight of calcium per million of water, in the form of soluble salts, usually sulphates, bicarbonates or chlorides, 3 pounds of sodium tetraphosphate or 3.6 pounds of potassium tetraphosphate, as made in accordance with our co-pending application aforesaid. As a result of this treatment the relatively large concentration of free calcium ions in the water is very greatly reduced or entirely eliminated by combining them into soluble only slightly ionized compounds or radicals due to the presence of the tetraphosphate. It will be found that in the softening of the water for steam boilers and feed lines the calcium and other similar compounds are prevented from being deposited to form a scale in the steam boilers and feed lines, notwithstanding the heating and concentration that takes place.

Similarly, the water may be softened in substantially the same way in connection with any of the other water softening operations, and particularly in the other industries listed above.

We have found that water may be softened in this way, in accordance with our process, much more effectively inasmuch as only three fourths as much by weight of the alkali metal tetraphosphate is required to completely soften the water as will be required of other materials previously used for such purposes. This can be readily demonstrated by a simple test of the water softening properties of these tetraphosphates. It is thus found that the alkali metal tetraphosphates are at least 33⅓% stronger and more effective for this purpose than in the case of metaphosphates, for example. This is demonstrated by the amount of the water softening substance required to be added to keep the calcium in solution. Furthermore, the tetraphosphates have been found to have a water softening effect increasing with the age of the solution for at least a day, while other water softeners do not increase their effectiveness with the increase of the time of application.

While we have described our invention above in detail we wish it to be understood that many changes may be made therein without departing from the spirit of the same.

We claim:

1. A process which comprises adding to hard water a water soluble salt of tetraphosphoric acid, $H_6P_4O_{13}$, so as to combine with an alkali earth metal to prevent the deposition of an alkali earth metal compound therein.

2. A process which comprises adding to hard water a water soluble salt of tetraphosphoric acid, $H_6P_4O_{13}$, so as to combine with calcium to prevent the deposition of a calcium compound therein.

3. A process of softening water, which comprises decreasing the free ion concentration of an alkali earth metal in hard water with a water-soluble salt of tetraphosphoric acid, $H_6P_4O_{13}$.

4. A process of softening water, which comprises decreasing the free ion concentration of an alkali earth metal in hard water with an alkali metal salt of tetraphosphoric acid, $H_6P_4O_{13}$.

5. A process of softening water, which comprises decreasing the free ion concentration of calcium in hard water with a water-soluble salt of tetraphosphoric acid, $H_6P_4O_{13}$.

6. A process of softening water, which comprises decreasing the free ion concentration of calcium in hard water with an alkali metal salt of tetraphosphoric acid, $H_6P_4O_{13}$.

AUGUSTUS H. FISKE.
CHARLES S. BRYAN.

APPELLANT'S EXHIBIT NO. 15.

85 MONSANTO CHEMICAL COMPANY ET AL

vs.

COE

Chemiker-Zeitung 47, p. 195

On the Behavior of Phosphoric Anhydride Toward Water. A direct Method of Preparation of Tetraphosphoric Acid

With hindsight on the peculiar character of the solution process of P_2O_5 in methyl and ethyl alcohol, it appeared that it would be interesting to study the behavior of P_2O_5 toward water, water being the theoretical first alcohol of the series of $C_nT_{2n}{+}_1OH$. This seemed to us to be timely, in as much as the question had not been touched upon as far as given in the literature.

For the preparation of orthophosphoric acid 27.4% P_2O_5 (based on water) is required. On reaching this limit, the reaction is no longer violent (the P_2O_5 was added in 0.5 g. portions), and the following portions go into solution only after 1 hour and the additions made until the quantity of anhydride reached 520%. There resulted a syrupy solution from which crystals of tetraphosphoric acid precipitated after five days. The formation of these crystals may obviously be represented by the following equation: $2H_3PO_4 + P_2O_5 = H_6H_4O_{13}$.

The tetraphosphoric acid is known as the third member of the series of condensed phosphoric acids of the general formula: $_n(H_3PO_4) - (_n\text{-}1)\ H_2O$; the first member of the series is pyrophosphoric acid. The condensed phosphoric acids are, with the exception of pyrophosphoric acid, only known in the form of their salts, and were especially investigated by Fleitmann and Henneberg. In the designated manner, that is directly from P_2O_5 and water, was the tetraphosphoric acid prepared. Until this time, it was obtained in the form of its salts by fusing different phosphates, for example, by fusing together the hexametaphosphate with the Pyro- or the ortho- phosphate:

$$Na_6P_6O_{18} + 3Na_4P_2O_7 = 3Na_6P_4O_{18}$$
$$Na_6P_6O_{18} + 2Na_3PO_4 = 2Na_6P_4O_{18}$$

Also the tetrapyrophosphoric acid may be obtained by fusing together the calculated quantities of ortho- and metaphosphates.

86 The free tetraphosphoric acid prepared by us has the following properties:

Properties	$H_6P_4O_{18}$	H_3PO_4	
m p.	34° C.	40° C.	The specific gravity of toluene was 0.8668 at 15° C.
D15° C. (Toluene = 1)	2.1217	2.1941	
D15° C. (H_2 = 1)	1.8886	1.8841	

The comparative determination of the specific gravity of tetra- and ortho- phosphate acids were made with a Gay-Lussac pycnometer, in which toluene was used as the density medium.

OJW MF

APPELLANT'S EXHIBIT NO. 16.

89 *Specification of Application Serial No. 438955*

To all Whom it May Concern:

Be It Known That We, Charles B. Durgin, Robert N. Foster and Charles F. Booth, citizens of the United States of America residing at Anniston in the County of Calhoun, and State of Alabama have invented certain new and useful improvements in Mixed Pyro and Meta Phosphates and Process for Producing the Same of which the following is a specification:

90 This invention relates to mixed pyro and meta phosphates of sodium, and has for its object the provision of a process for producing such mixtures which shall have a predetermined hydrogen ion concentration in their aqueous solutions.

It has long been known that mixtures of the various ortho sodium phosphates could be used to establish a definite hydrogen ion concentration in aqueous solutions. This has been made use of in the treatment of boiler waters where the phosphate radicle served as a precipitating agent to precipitate the positive ion of various undesirable salts of the alkaline earth group metals from solution, this effect taking place in a solution which was maintained at a hydrogen ion concentration which was not injurious to the boiler steel. In some cases it is desirable to employ as a precipitating agent, mixed pyro and meta phosphates which will give the desired alkalinity to boiler water and at the same time exhibit a delayed precipitating action towards the alkaline earth metal salts. The pyro and meta phosphates are especially well suited for this purpose, since they do not immediately hydrate to the orthophosphates and hence do not immediately precipitate insoluble orthophosphates.

We have found that mixtures of tetrasodium pyrophosphates and meta sodium phosphates are particularly suitable for this purpose, since by varying the proportions of each, any desired hydrogen ion concentration between the limits of pH 6.4 and about 10 may be obtained.

91 We have furthermore found that readily soluble mixtures of pyro and meta sodium phosphate of a predetermined hydrogen ion concentration, may be produced by heating to the fusion point appropriately proportioned mixtures of sodium ortho phosphates or mixtures of orthophosphoric acid and the sodium salt of a replaceable acid and then rapidly cooling. Suitable sodium salts for this purpose are the chloride and the carbonate of sodium, although others may be used. The latter compound is preferable since it is difficult when producing mixtures high in tetrapyrophosphate content to expel all of the chlorine from the melt.

The accompanying graphical representation sets forth the relation between the various proportions of tetrasodium pyrophosphate and sodium meta phosphate in the melt, and the pH of a 1% aqueous solution of these mixtures as we have found them to be. The melting points of these mixtures are also given on this drawing.

92 Our invention will be illustrated by the following examples:

Example 1.

Mix together 76.5 lbs. of monosodium orthophosphate ($Na\ H_2\ PO_4.2H_2\ O$) and 134.7 lbs. of disodium orthophosphate ($Na_2\ H\ PO_4\ 12H_2\ O$).

Heat to the melting point of the mixture which is at a temperature of approximately 620°C. When a uniform melt has been obtained, cool quickly by pouring the molten mass on a cold metal surface in thin layers. The layers of molten salt should not be over ¾ inch thick and preferably less than ½ inch thick. The metal surface on which the molten salt is poured, if in substantially continuous use as in the case of continuously operated chill rolls, may be water cooled in order that accumulated heat may be carried away rapidly. We have found that water at ordinary temperatures is preferably. However, it is possible to operate satisfactorily when cooling with water at or near its boiling point.

We have found that it is particularly desirable to cool rapidly during the first portion of the cooling period. For example, the maximum benefit from quick cooling is obtained by cooling from the melting point to say in the neighborhood of 100 to 300°C. If this is done rapidly, then it is not necessary that the remainder of the cooling be at so rapid a rate. For the purpose of this specification, we shall designate as "quickly cooling", both the processes of cooling at a rapid unbroken rate from the original to the final temperature, and the process of cooling at a rapid unbroken rate from the original to an intermediate temperature, followed by cooling at a different rate (either faster or slower) than the original rate.

93 The product from the melt as above designated, Example 1, is approximately 100 lbs. of a solid con-

sisting of 50% tetrasodium pyrophosphate and 50% sodium meta phosphate. A sample of this material in water to make a 1% solution will show a pH of approximately 8.6.

The reactions for stoichiometrically determining the proportions in this example are:

$$\mathrm{Na\,H_2\,PO_4\,.2H_2\,O = Na\,PO_3 + 3H_2O}$$
$$\mathrm{2Na\,H\,PO_4\,.12H_2O = Na_4P_2O_7 + 25H_2O}$$

Example 2.

Mix together 74.14 lbs. of sodium carbonate (soda ash) and 78.26 pounds of phosphoric acid $H_3\,PO_4$ (or 104.2 lbs. of 75% $H_3\,PO_4$). Heat slowly as long as carbon dioxide and water vapor are evolved, then raise the temperature gradually to the melting point, which is approximately at a temperature of 940°C. Heating may be carried out in a carbon crucible or in a fire brick hearth heated by radiation. When a uniform melt has been obtained, cool the melt quickly as described in the previous example. Approximately 100 lbs. of a mixture of 80% tetrasodium pyrophosphate and 20% of sodium meta phosphate will be obtained. A sample of this material in water so as to make a 1% solution will show a pH in the neighborhood of 9.5.

The reaction for stoichiometrically determining the proportions in this example are:

$$\mathrm{Na_2\,Co_3 \quad 2\,H_3\,PO_4 = 2\,Na\,PO_3 + CO_2 + 3\,H_2O}$$
$$\mathrm{2\,Na_2\,CO_3 + 2\,H_3\,PO_4 = Na_4\,P_2\,O_7 + 2\,CO_2 + 3H_2O}$$

94 The examples above illustrate two ways by which two different mixtures of tetrasodium, pyrophosphate and sodium meta phosphate may be made. Obviously any one method might be used for both mixtures, as well as other mixtures not specifically mentioned. In general, it may be said that the results of both methods yield a very similar product, hence it becomes an economic question of choice of raw materials as to which method is employed.

The proportioning of the raw materials is done on a simple stoichiometrical basis as indicated which is familiar to a person skilled in the art.

Fusion may be carried out in each instance in an ordinary carbon or graphite crucible or it may be done on a brick hearth with reverberatory heating.

Mixtures of these two salts containing between 50 and 100% of sodium meta phosphate and 50 to 0% sodium tetra pyrophosphate, on being quickly cooled from the melting point as above described, are clear glass like solids and do not exhibit a sharp freezing point, being presumably supercooled solids. Mixtures containing from 50 to 100% sodium tetrapyrophosphate and 50 to 0% sodium meta phosphate, exhibit a gradually increasing crystalline fracture and a sharper freezing point, the mixture at the same time becoming more and more translucent as the tetra pyrophosphate content approaches 100%.

1. A process of producing a mixture of tetra sodium pyrophosphate, and meta-sodium-phosphate, which consists in mixing a sodium salt with a phosphorus compound containing the elements of water, raising the temperature to the melting point and quickly cooling the resulting product.

2. Process of producing a mixture of tetrasodium pyrophosphate and meta sodium pyrophosphate consisting in mixing stoichiometrically proportioned amounts of sodium carbonate and orthophosphoric acid, heating said mixture to the melting point, then cooling the mass.

3. Process of producing a mixture of tetrasodium pyrophosphate and meta sodium phosphate consisting in mixing stoichiometrically proportioned amounts of sodium carbonate and orthophosphoric acid, heating said mixture to the melting point, then quickly cooling the mass.

4. Process of producing a mixture of tetrasodium pyrophosphate and meta sodium phosphate, having a predetermined hydrogen ion concentration in its aqueous solution consisting in mixing stoichiometrically proportioned amounts of sodium carbonate and orthophosphoric acid, heating said mixture to the melting point and cooling the mass.

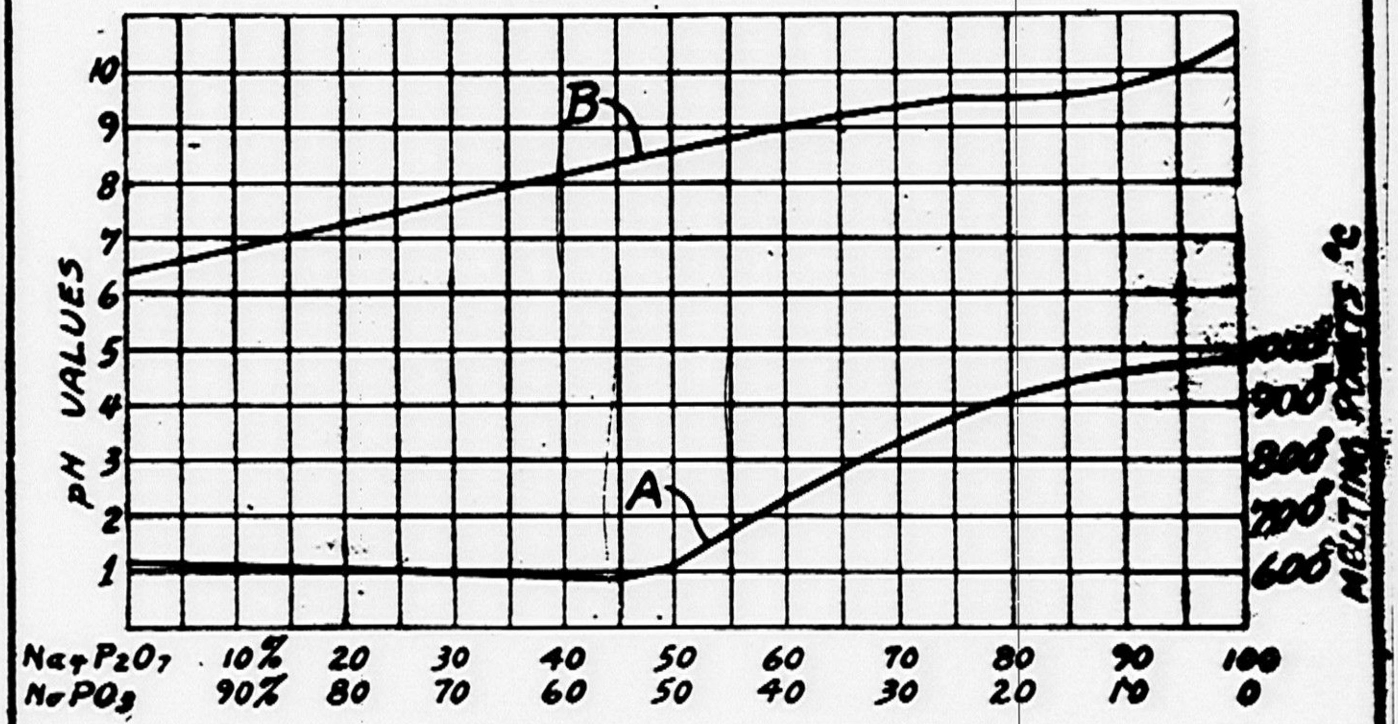
5. Process of producing a mixture of tetrasodium pyrophosphate and meta sodium phosphate having a predetermined hydrogen ion concentration in its aqueous solution consisting in mixing stoichiometrically proportioned amounts of sodium carbonate and orthophosphoric acid, heating said mixture to the melting point and quickly cooling the mass.

96 6. As a new composition of matter, a homogeneous mass of tetra sodium pyrophosphate and sodium meta phosphate.

7. As a new composition of matter a homogeneous mass of tetrasodium pyrophosphate and sodium meta phosphate exhibiting a pH between the limits of 6.4 and 10 in its 1% aqueous solution.

8. As a new composition of matter, a fused homogeneous mass of tetra sodium pyrophosphate and sodium meta phosphate, said mixture being glass like when the tetra pyrophosphate content is less than about 50% and gradually becoming translucent as the tetrapyrophosphate content increases.

* * * * * * * * * *



A – MELTING POINTS OF MIXTURES OF TETRA-PYRO & METASODIUM PHOSPHATE.

B – pH VALUES OF 1% AQUEOUS SOLUTIONS OF MIXTURES OF TETRA PYRO & METASODIUM PHOSPHATE.

INVENTORS
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R. N. Foster
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BY
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ATTORNEYS

WITNESS
Charles H. Cassetto

APPELLANT'S EXHIBIT NO. 17.

102 *Specification of Application Serial 733,392*

To All Whom It May Concern:

Be it known that we, Charles B. Durgin, Robert N. Foster, and Charles F. Booth, citizens of the United States, residing at Anniston, County of Calhoun, in the State of Alabama, have invented certain new and useful improvements in Soluble Dehydrated Sodium Phosphates and Process for Producing Same, of which the following is a specification:—

103 The present application is a continuation in part of our prior application filed March 26, 1930; Serial No. 438,955.

This invention relates to dehydrated phosphates of sodium and particularly to such phosphates from which the water of constitution has been driven and to a process for producing such phosphates. It has for its object the provision of an improved water softening and scale inhibiting compound which shall have a predetermined hydrogen ion concentration in its aqueous solution and which shall have pronounced buffering properties in such solution. A further object is the provision of a water-treating compound which shall have pronounced properties for the retention in solution of the common alkaline—earth metals and compounds thereof.

It has long been known that mixtures of the various ortho-sodium phosphates could be used to establish a definite hydrogen ion concentration in aqueous solution. This has been made use of in the treatment of boiler waters and of detergent solutions where the phosphate radicle served as a precipitating agent to precipitate the positive ion of the various undesirable salts of the alkaline earth group metals from solution, this effect taking place in a solution which was maintained at a hydrogen ion concentration which was not injurious to the boiler steel, or which was suitable for the various detergent uses in which such salts were em-

ployed. In some cases it is desirable to employ as a water treating agent pyro and meta phosphates which will give the desired alkalinity to boiler water and at the same time exhibit a delayed precipitating action towards the alkaline earth metal salts present in natural waters. The pyro and meta phosphates are especially well suited for this purpose, since they do not immediately hydrate to the orthophosphates and hence do not immediately precipitate insoluble ortho-phosphates. For some purposes a greater de-
lay in the rapidity of the reversion of such meta or
104 pyro phosphates to the ortho-phosphates is desirable
and it is a further additional object of the present invention to provide a dehydrated phosphate product, which exhibits an increased resistance to reversion.

We have found that mixtures of tetrasodium pyrophosphate and sodium meta phosphate fused together and chilled to form an amorphous glass-like soluble, dehydrated phosphate product are particularly suitable for the present purpose. By varying the constituents of the product any desired hydrogen ion concentration between the limits of $pH = 6.4$ to $pH = 10.2$ may be obtained.

We have furthermore found that readily soluble mixtures of molecularly dehydrated sodium phosphates of a predetermined hydrogen ion concentration may be obtained by heating to the fusion point appropriately proportioned mixtures of sodium ortho-phosphates, or mixtures of orthophosphoric acid and the sodium salt of a replaceable acid and then rapidly cooling. Suitable sodium salts for this purpose are the chloride and carbonate of sodium, although others may be used. The latter compound is preferable since it is difficult, when producing mixtures having a high alkali content to expel all of the chlorine from the melt.

In the accompanying drawings, Figure 1 shows certain solubility relationships of the sodium and potassium series of dehydrated phosphates. Figure 2 shows the hydrogen ion concentration of the sodium phosphates prepared by our process. Figure 3 shows the hydrogen ion concentration of the dehydrated potassium phosphates. Figure 4 illustrates the solubility of the sodium and potassium series of phosphates in concentrated solutions. In Figure 5 is given the melting points of the sodium phosphates.

Our invention will be illustrated by the following examples:—

Example 1

Mix together 76.5 lbs. of mono-sodium ortho-phosphate ($NaH_2PO_4 .2H_2O$) and 134.7 lbs. of di-sodium ortho-phosphate ($Na_2HPO_4 .12H_2O$). Dehydrate and heat in a gas fired reverberatory furnace to the melting point of the mixture which is at a temperature of approximately 620°C. When a uniform melt has been obtained, cool quickly by pouring the molten mass on a cold metal surface in thin layers. The layers of molten salt should not be over ¾ inch thick and preferably less than ½ inch thick. The metal surface on which the molten salt is poured, if in substantially continuous use as in the case of continuously operated chill rolls, may be water cooled in order that accumulated heat may be carried away rapidly. We have found that water at ordinary temperatures is preferable. However, it is possible to operate satisfactorily when cooling with water at or near its boiling point.

We have found that it is particularly desirable, in order to develop the amorphous condition, to cool rapidly during the first portion of the cooling period. For example, the maximum benefit from quick cooling is obtained by cooling from the melting point to say in the neighborhood of 100 to 300°C. If this is done rapidly, then it is not necessary that the remainder of the cooling be at so rapid a rate. For the purpose of this specification, we shall designate as "quickly cooling", both the process of cooling at a rapid unbroken rate from the original to the final temperature, and the process of cooling at a rapid unbroken rate from the original to an intermediate temperature, followed by cooling at a different rate (either faster or slower) then the original rate.

The product from the melt as above designated, Example 1 is approximately 100 lbs. of a solid consisting theoretically of 50% tetrasodium pyro-phosphate and 50% sodium meta phosphate. A sample of this material as produced in commercial operation and dissolved in water to make a 1% solution will show a pH of approximately 8.6. See Curve C′ of Figure 2.

106 The reactions for stoichiometrically determining the theoretical proportions in this example are:

$$NaH_2PO_4.2H_2O = NaPO_3 + 3H_2O$$
$$2(Na_2HPO_4.12H_2O) = Na_4P_2O_7 + 25H_2O$$

Example 2

Mix together 74.14 lbs. of sodium carbonate (soda ash) and 78.26 pounds of phosphoric acid, H_3PO_4 (or 104.2 lbs. of 75% H_3PO_4). Heat slowly in a gas fired reverberatory furnace as long as carbon dioxide and water vapor are evolved, then raise the temperature gradually to the melting point, which is approximately at a temperature of 940°C. Heating may be carried out in a carbon crucible or on a fire-brick hearth heated by radiation. When a uniform melt has been obtained, cool the melt quickly by pouring it on a cooled metal surface as described in the previous example. Approximately 100 lbs. of a mixture having a theoretical composition consisting of 80% tetra sodium pyro-phosphate and 20% of sodium meta phosphate will be obtained. A sample of this material as produced in commercial operation and dissolved in water so as to make a 1% solution will show a pH in the neighborhood of 9.5. See Curve C′ of Figure 2.

The reactions for stoichiometrically determining the theoretical proportions in this example are:

$$Na_2CO_3 + 2H_3PO_4 = 2NaPO_3 + CO_2 + 3H_2O$$
$$2Na_2CO_3 + 2H_3PO_4 = Na_4P_2O_7 + 2CO_2 + 3H_2O$$

The examples above illustrate two ways by which two of our improved dehydrated phosphates may be made. Obviously any one method might be used for both mixtures, as well as other mixtures not specifically mentioned. In general, it may be said that the results of both methods applied to any one mixture yield a very similar product, hence it becomes an economic question of choice of raw materials as to which method is employed.

107 The proportioning of the raw materials is done on a simple stoichiometric basis as indicated which is familiar to persons skilled in the art.

Fusion may be carried out in each instance in an ordinary carbon or graphite crucible or it can be done on a brick hearth with reverberatory heating.

Mixtures of these two salts containing stoichiometrically between 50% and 100% of sodium meta phosphate and 50% to 0% tetrasodium pyro-phosphate, on being quickly cooled from the melting point as above described, are clear amorphous glass-like solids as distinguished from crystalline bodies and do not exhibit a sharp freezing point, being presumably super-cooled liquids. Mixtures containing stoichiometrically from 50% to 100% of tetra-sodium pyro-phosphate and 50% to 0% sodium meta phosphate, exhibit a gradually increasing crystalline fracture and a sharper freezing point, the mixture at the same time becoming less and less transparent as the theoretical tetra-sodium pyrophosphate content approaches 100%.

When carrying out our process on an industrial scale, heating of the phosphate salts or mixtures of suitable salts and phosphoric acid, is preferably carried out in a reverberatory furnace with gas heating. In such cases we have found that the product formed by our process contains a relatively small proportion i.e., less than 5% ortho and acid pyro-phosphate. The presence of this impurity in our fused mixtures is probably due to the presence of water vapor in the combustion gases and also, in past, due to the rapidity of the heating and melting operation as carried out on such a scale. The presence of this small amount of impurity is immaterial in the various uses in which the product is employed, its effect being merely to change somewhat the hydrogen ion concentration of the solutions which are prepared therefrom.

108 For this reason we have shown on Figure 2 of the accompanying drawing two curves labeled C and C′. Curve C has been prepared from the sodium phosphates by first carefully dehydrating the material in an electric furnace at temperatures at which the meta phosphate is known to form and then raising the temperature to the fusion point of the mixture. Curve C′ is representative of material which has been industrially prepared by fusion in the presence of water vapor in an industrial furnace. By varying the conditions of dehydration of the ortho-phosphates some variation can be made in the acidity relations of the products formed therefrom. It may be said that in general the range of hydrogen ion concentrations obtained by products produced according to our process will lie between the values given by Curves C and C′ on Figure 2.

In the above description we have referred to the composition as containing "theoretically" or "stoichiometically" a certain amount of sodium meta phosphate and tetrasodium pyro-phosphate. We have used this terminology because although the stoichiometric proportions are based upon the presence of three two compounds, a chemical examination of our new product indicates that these compounds have in some cases lost their chemical identity, while in other cases such chemical identity has been extensively altered.

This may be illustrated by the following test.

If a solution be prepared by dissolving in water a fused mixture containing the 60% sodium meta phosphate and 40% tetra-sodium pyro-phosphate equivalent and the solution then tested for pyro-phosphate content according to the method of Britake and Dragunov, J. Chem. Ind. Moscow, 4, 49151 (1927) Chem. Abstr. 22 2900 (1928), a surprising result is obtained.

On the addition of zinc sulphate to the neutralized solution no precipitate is formed. On the other hand if a mechanical mixture as distinct from a fused mixture and

having the same theoretical proportions as that given above is similarly tested, a heavy precipitate of zinc pyro-phosphate is obtained. This test shows that zinc
109 pyro-phosphate can be precipitated from a solution of the mechanical mixture while no such precipitate is formed in a solution of the fused mixture. This indicates that the pyro-phosphate content has lost its chemical identity in the fused mixture, and while such mixture contains the stoichiometric alkali and acid equivalent of the pyro-phosphate it no longer behaves chemically as if such pyro-phosphate were present.

In the same manner it can be demonstrated that in certain of the compositions the meta phosphate had also lost its identity. This may be determined by testing solutions of mechanical mixtures of the sodium meta phosphate and tetra-sodium pyro-phosphate in comparison with fused mixtures of the same equivalent composition.

The solutions of the mechanical mixtures of these salts will give characteristic heavy precipitates of meta phosphate with silver nitrate and barium chloride. The solutions of the fused mixtures show either no precipitate or only a small amount, depending on the composition.

These chemical tests indicate that fused mixtures of the two salts no longer contain meta-phosphate or pyro-phosphate as such and hence differ from known compositions of the prior art.

An important distinction between our compositions and known compositions or compositions which might ordinarily be considered as equivalents thereof resides in the ready solubility of our product as compared with such other compositions. Such a property is important since one of the important applications of our product has to do with the treatment of water for various purposes.

Two types of solubility effect will be illustrated, i.e. the preparation of dilute solutions and the preparation of concentrated solution.

Such solutions of our dehydrated and fused sodium phosphates may be prepared by dissolving a proportion of the phosphate directly in water. For example a 1% solution is prepared by adding 1% of the solid dehydrated sodium phosphate to 99% of water. Any and all of the phosphates prepared according to our process and ranging in equivalent composition between say 99% sodium metaphosphate and 1% tetra-sodium pyro-phosphate to 1% sodium meta phosphate and 99% tetrasodium pyrophosphate can be utilized in this manner to form a 1% solution, as shown in line A of Figure 1.

As contrasted with this property of the sodium salts, we have found that the dehydrated and fused potassium salts do not form 1% solutions in all proportions throughout the series. If 1% of the corresponding solid dehydrated potassium salts are placed in contact with 99% of water, the solid phase will not dissolve completely. The extent of solubility of the dehydrated potassium phosphate series is shown as line B in Figure 1. The hydrogen ion concentration of the 1% solution of the sodium salts is shown in Figure 2 while the same data are given in Figure 3 for such solutions of the potassium salts as were formed under similar conditions. It will be understood, however, that the latter data are not given for 1% solutions because of the impossibility of forming such solutions.

Concentrated Solutions

Saturated solutions of these dehydrated sodium phosphates were prepared by mixing together water and any of the sodium phosphate compositions herein described in such proportions that some solid phase is present in the solution after equilibrium has been attained. We have found that the composition of the solution differed from that of the solid phase in equilibrium with said solution. This indicates a differential or selective solubility effect in which one or more constituents of the solid tend to dissolve while others tend to remain undissolved.

111 The nature of this solubility effect is shown on Figure 4 by Curve E. From these data it will be seen that high solubility i.e., over 50% total solids is obtained in the dehydrated sodium phosphate series in the range between about 99% and slightly less than 50% equivalent sodium meta phosphate content, while if less than 50% sodium meta phosphate is present the solubility of the salt rapidly declines, reaching a minimum of approximately 6% for the compound $Na_4P_2O_7$.

In the case of the potassium series the solubility effect as measured by the total solid dissolved in concentrated solutions is exactly reversed. In this case salt mixtures having a high content of potassium meta phosphate are relatively insoluble, the solubility of the series increases as the content of tetra-potassium pyro-phosphate increases and reaches the highest value of the series for the pure compound, $K_4P_2O_7$. The solubility of the series of dehydrated potassium phosphates is given on Curve F of Figure 4.

In connection with our experiments on the differential or selective solubility of the dehydrated sodium and potassium phosphates we have made the following additional observations:—

Selective Solubility in the Dehydrated Phosphate Series

Our experiments show that when mixtures of water and members of the sodium series of phosphates are made under conditions so that some solid phase remains in contact with the solution after equilibrium that practically all of the constituent stoichiometrically equivalent to meta phosphate is dissolved and the solid phase is almost entirely composed of the constituent stoichiometrically equivalent to tetra sodium pyro-phosphate. In other words in the sodium series as herein prepared the sodium meta phosphate equivalent is the soluble constituent. The tetra sodium pyro-phosphate equivalent is in no case completely dissolved.

112 In the potassium series the conditions are exactly reversed. In this series the pyrophosphate constituent of the fused mixtures is completely dissolved throughout most of the range of compositions. The potassium meta phosphate constituent is in no case completely dissolved. Such properties are of importance as indicating a definite absence of equivalency in the sodium and potassium series of fused dehydrated phosphates.

It has previously been proposed to utilize mixtures of the pyro-phosphate and meta phosphate for the treatment of water for boiler use. Such mixtures, however, present the following objections.

The mechanical or loose mixtures are difficult to maintain in uniform condition throughout the mass of the mixture. This is so because the meta phosphate is obtained as fairly large pieces resembling broken glass while the pyrophosphate is either in crystalline form or in a finely ground condition. It is undesirable to grind the materials because the former is hygroscopic and readily becomes sticky and gummy if exposed to air of ordinary humidity. Even though a uniform powder could be prepared at the factory, shipment and the attendant handling of the mixture before use would tend to segregate one material from the mass and make the preparation of a definite solution of the material a difficult one.

We have furthermore determined that our fused homogeneous mixtures have a lower pH than mechanical or loose mixtures having the same original stoichiometric composition. For example a fused mixture containing the equivalent of 80% meta and 20% tetra pyro-phosphate in 1% solution has a pH of 7.5, a 60% meta 40% tetra-pyrophosphate has a pH of 8.0 while a 40% meta 60% tetrapyrophosphate has a pH of 8.7. The pH of corresponding mechanical mixtures have values of 8.6; 9.1 and 9.4 respectively. From the above values we see that the fused mixtures have a greater acidity than the mechanical mixtures of from 0.7 to 1.1 pH units, all of which points to a greater alkali neutralizing capacity inherent in our improved product.

113 Further study of our improved product shows that we obtain a greater buffering action, in other words a greater reserve acidity than is obtained by simple mixtures of the meta phosphate and tetra-pyro-phosphate. This is confirmatory of the findings mentioned above which indicate a greater alkali neutralizing capacity. The buffering property is of value in other ways than those mentioned and this property will be found of value by those skilled in the art.

A further valuable property possessed by our fused dehydrated sodium phosphates is the enhanced water softening properties. Since it has already been proposed to soften water utilizing the meta phosphate, the properties of such phosphate in preventing the precipitation of the alkaline earth metal compounds are more or less well known. We have now found that solutions formed from fused mixtures, the equivalent of meta and pyro-phosphate in stoichiometric proportions, have the porperty of producing zero hardness using a considerably lesser proportion of our phosphate product than of an equivalent mechanical mixture.

Since it has been proposed to prepare solutions of mixtures of the two constituents namely the meta and tetra-pyro-phosphate, the relative rates of solution of corresponding mixtures of our fused product are of importance. In comparative tests with our fused homogeneous product and mechanical mixtures of equivalent stoichiometric composition we have found that our improved phosphates dissolve completely and in a relatively short time while the mechanical mixtures of equivalent composition require an inordinately long time for complete solution.

We have also noted, in this connection, that our product causes a lesser degree of corrosion on the dissolving equipment. This is believed to be due to the fact that the constituents of our product dissolve completely at a uniform rate provided sufficient water is presnt to form a complete solution, we have also noted that the acidity of the solution is at no time excessively high due to the acid constituent dissolving at a faster rate. This is a factor of considerable importance because of the universal use of iron dissolving equipment in water treating operations.

114 *Optical Properties of the Dehydrated Sodium Phosphates*

Sodium meta phosphate is an isotropic material having a refractive index of 1.480 plus or minus 0.002, for ordinary light.

Tetra-sodium pyro-phosphate crystals are biaxial and positive and have a small axial angle. The indices are:

alpha = 1.473 plus or minus 0.002
gamma = 1.494 plus or minus 0.002

The crystals are orthorhombic, platy in shape, and have a negative elongation.

Compositions stoichiometrically equivalent to a content of approximately 50 percent of sodium meta phosphate and 50 percent of tetra-sodium pyro-phosphate are mostly isotropic amorphous solids having an index of refraction of 1.480 plus or minus 0.002. There are a few anisotropic, biaxial crystals visible in the isotropic amorphous solid. Compositions ranging in content between the 50-50 composition mentioned above and a composition containing the stoichiometric equivalent of 90 percent sodium meta phosphate and 10 percent of tetra-sodium pyro-phosphate, have the same refractive index as that mentioned for the 50 - 50 composition and show fewer crystalline inclusions.

Compositions of our products ranging between the stoichiometric equivalent of 50 percent sodium meta phosphate and 50 percent of tetra-sodium pyro-phosphate to the 90 percent tetra-sodium pyro-phosphate and 10 percent sodium meta phosphate compositions show a gradually increasing anisotropic biaxial crystalline content in the amorphous solid. The crystalline phase appears as plate-like or feathery crystals with the amorphous isotropic material between the crystals. The insotropic material has an index of 1.480. The crystalline phase has the optical properties of the tetrasodium pyro-phosphate given above—that is the crystals are anisotropic and biaxial.

The optical examination of our improved product indicates therefore that those compositions having a major proportion of equivalent sodium meta phosphate consist of a homogeneous amorphous isotropic solid having a refractive index between the limits of 1.478 and 1.482 in which isotropic solid is suspended a relatively small proportion of anisotropic crystalline material.

115 The proportion of crystalline material in our product is present in smaller proportion than that indicated by the stoichiometric composition of the mass. This clearly indicates that a chemical combination of the constituents present has occurred which combination results in the formation of a new compound characterized by the properties given above. Such a conclusion agrees with the chemical properties which have already been mentioned.

Because of the complexity of the dehydrated sodium phosphates obtained by our process we are unable to more accurately define them. Since they are definitely reproducible by following the methods outlined in our disclosure above they are properly defined and characterized by the methods stated.

Having now particularly described our invention and the manner in which it may be worked, it will be apparent that our invention is susceptible of various changes and modifications without departing from the spirit thereof, and we desire therefore that our invention be not limited except as indicated by the prior art or as particularly pointed out in the claims.

116 What we claim is:

1. A water soluble fused homogenous composition comprising molecularly dehydrated sodium phosphates corresponding stoichiometrically to a mixture of tetra-sodium pyro-phosphate and sodium metaphosphate, in which each of the components is present in substantial proportions, said composition being completely soluble in water when only 1% of the composition is added thereto.

2. A water soluble fused homogeneous composition comprising molecularly dehydrated sodium phosphates corresponding stoichiometrically to a mixture of tetra-sodium pyro-phosphate and sodium meta-phosphate components in which each of the said components is present in proportions above 1%.

3. A fused homogeneous mixture of molecularly dehydrated sodium phosphates corresponding stoichiometrically to a mixture of tetra-sodium pyro-phosphate and sodium meta-phosphate components in which each of the said components is present in proportions above 10 percent and which is capable of forming a solution of more than 50% concentration where the sodium meta-phosphate stoichiometrically present is above 48%.

4. A fused homogeneous completely water soluble mixture of molecularly dehydrated sodium phosphates comprising stoichiometrically sodium meta-phosphate and tetra-sodium pyro-phosphate components in which there is present at least 1% of each of the said components.

5. A series of fused homogeneous compositions of molecularly dehydrated sodium phosphate each member comprising stoichiometrically a substantial proportion of both sodium meta-phosphate and sodium pyro-phosphate in which series that composition has high solubility in the region where a major proportion of sodium meta-phosphate is present in said composition.

117 6. A water soluble mixture of molecularly dehydrated sodium phosphates corresponding stoichiometrically to a mixture of sodium meta and sodium pyrophosphates and in which the pyro-phosphate has lost its chemical identity.

7. A water soluble, molecularly dehydrated sodium phosphate compound corresponding stoichiometrically to a mixture of sodium meta and sodium pyro-phosphates and in which the meta phosphate has lost its chemical identity.

8. A water soluble molecularly dehydrated sodium phosphate compound corresponding stoichiometrically to a mixture of sodium meta and sodium pyro-phosphate, said mix-

ture containing between 1 and 50% equivalent meta phosphates and being capable of forming a concentrated solution in water.

9. A water soluble completely fused molecularly dehydrated sodium phosphate compound, comprised stoichiometrically of a mixture of sodium meta and tetra-sodium pyro-phosphate, said mixture containing between 1% and 50% of sodium meta phosphate equivalent, the remainder being substantially the stoichiometric equivalent of tetra-sodium pyro-phosphate.

10. A completely fused molecularly dehydrated sodium phosphate compound comprising a major portion of a highly water soluble constituent stoichiometrically equivalent to sodium meta phosphate and a minor proportion of a less soluble constituent stoichiometrically equivalent to tetra-sodium pyro-phosphate.

11. A glass-like molecularly dehydrated sodium phosphate compound comprising a relatively large proportion of a highly soluble constituent stoichiometrically equivalent to sodium meta phosphate, and a minor proportion of a less soluble constituent stoichiometrically equivalent to tetra-sodium pyro-phosphate.

118 12. A molecularly dehydrated water soluble sodium phosphate compound formed by mixing together proportions of mono and di-sodium ortho-phosphate, heating the mixture to completely fuse the same and then quickly cooling the melt.

13. A completely fused molecularly dehydrated, water soluble sodium phosphate compound formed by mixing together the sodium salt of a replaceable acid and phosphoric acid, heating the mixture to the fusion point of the dehydrated compound and then quickly cooling the melt.

14. A homogeneous molecularly dehydrated sodium phosphate compound comprising a highly water soluble constituent stoichiometrically equivalent to sodium meta phosphate and a less soluble constituent stoichiometrically equivalent to tetra-sodium pyro-phosphate, each of said constituents being present in amounts greater than one percent.

15. A homogeneous molecularly dehydrated water soluble sodium phosphate compound comprising a glass-like solid containing an isotropic constituent having a refractive index between the limits of 1.478 and 1.482.

16. A homogeneous molecularly dehydrated water-soluble composition comprising an amorphous isotropic constituent having a refractive index between the limits of 1.478 and 1.482.

17. A homogeneous molecularly dehydrated, water-soluble composition comprising a major proportion of an amorphous isotropic constituent having a refractive index between the limits of 1.478 and 1.482.

119 18. A homogeneous molecularly dehydrated, water-soluble composition comprising a major proportion of an isotropic cnstituent having a refractive index between the limits of 1.478 and 1.482 and a minor proportion of an anisotropic constituent.

19. A homogeneous molecularly dehydrated, water-soluble composition comprising a minor proportion of an isotropic constituent having a refractive index between the limits of 1.478 and 1.482 and a major proportion of an anisotropic biaxial positive crystalline constituent having a negative elongation.

20. A process for producing a homogeneous molecularly dehydrated water-soluble sodium phosphate comprising mixing together a sodium salt of a replaceable acid and phosphoric acid, heating the mixture to the fusion point of the dehydrated phosphate completely fusing the same and quickly cooling the melt.

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Print of drawing as originally filed

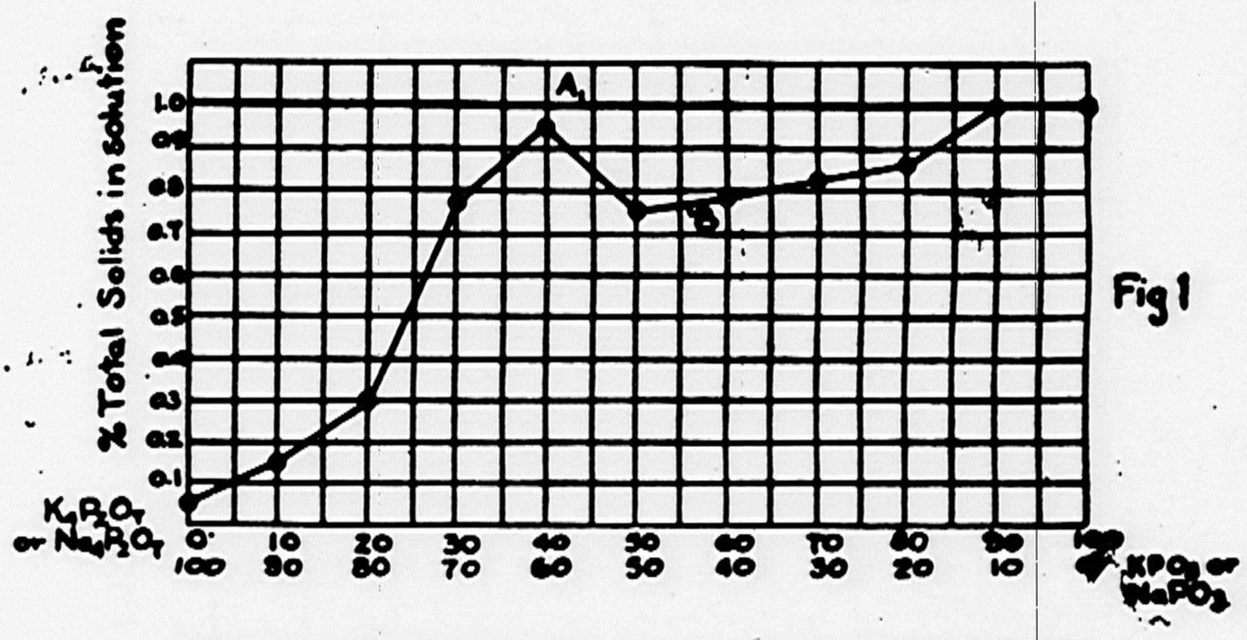

Fig 1

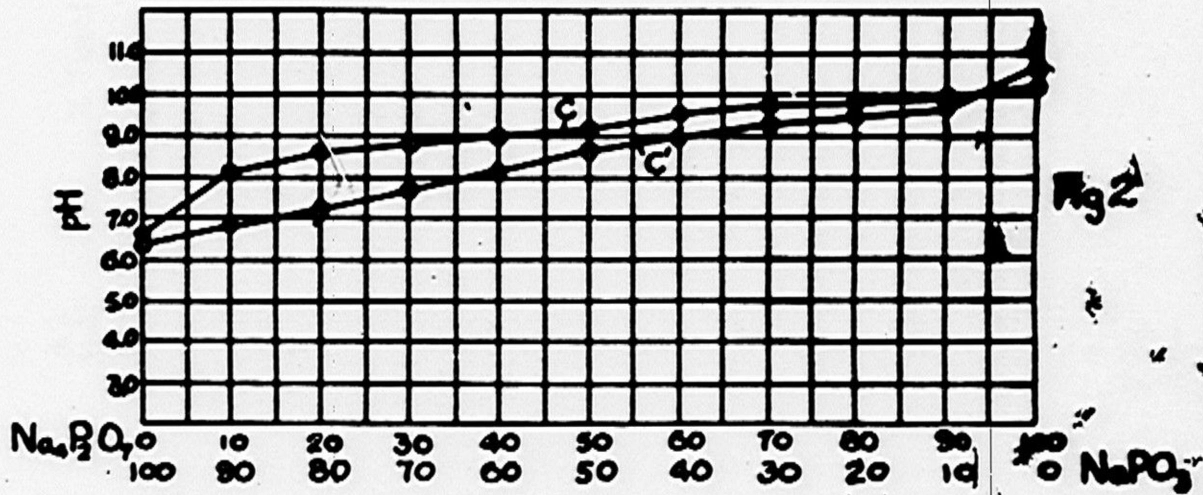

Fig 2

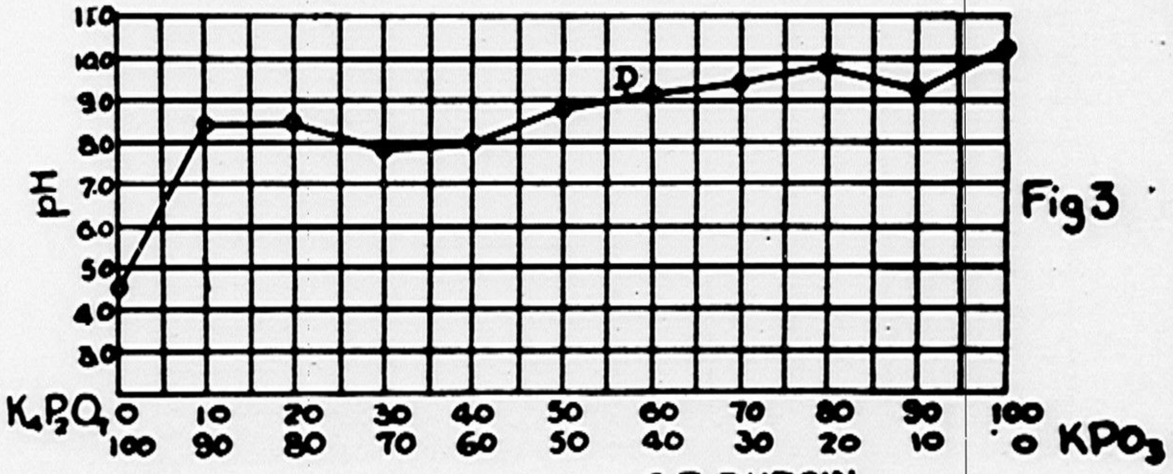

Fig 3

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Print of drawing as originally filed.

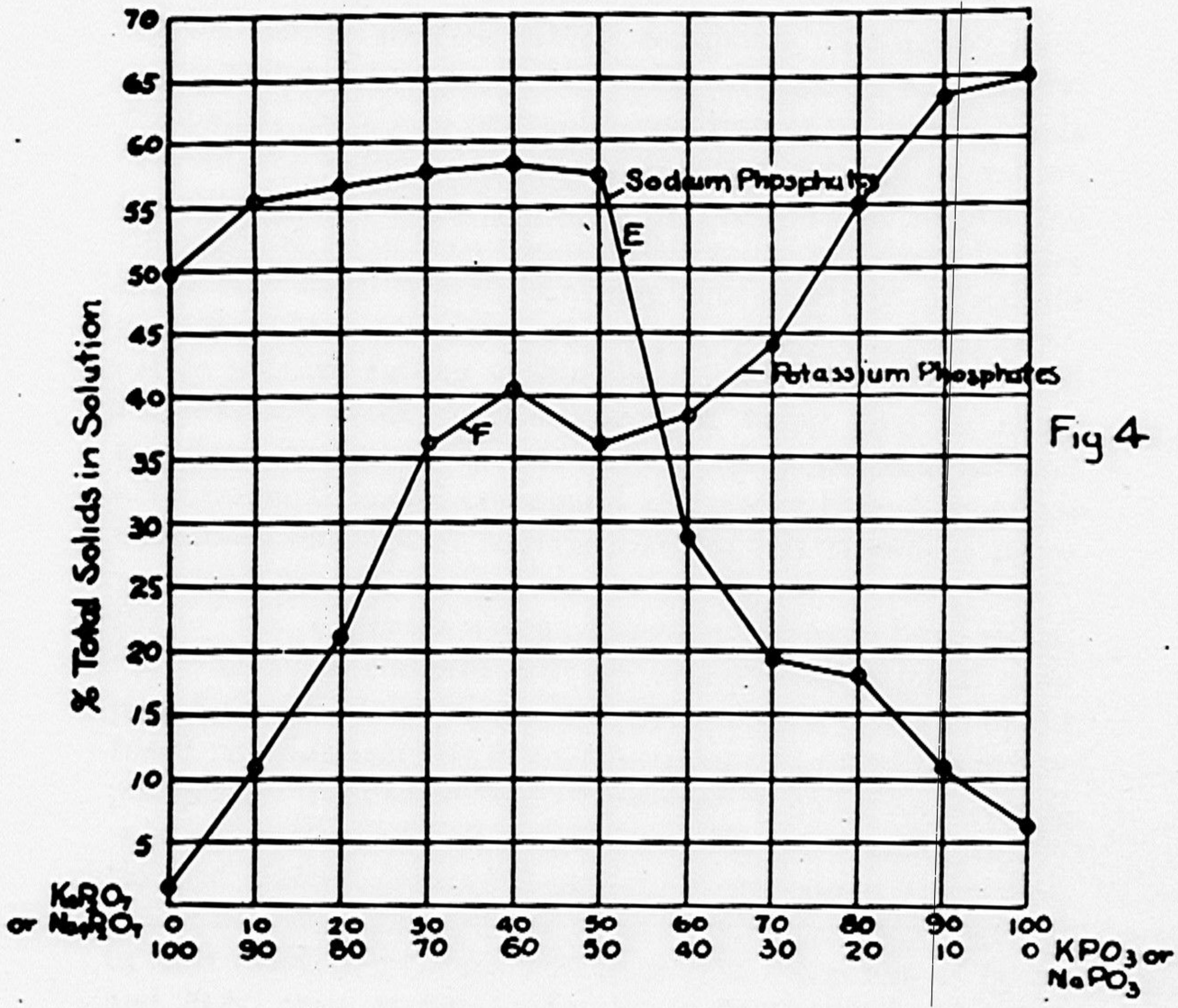

Fig 4

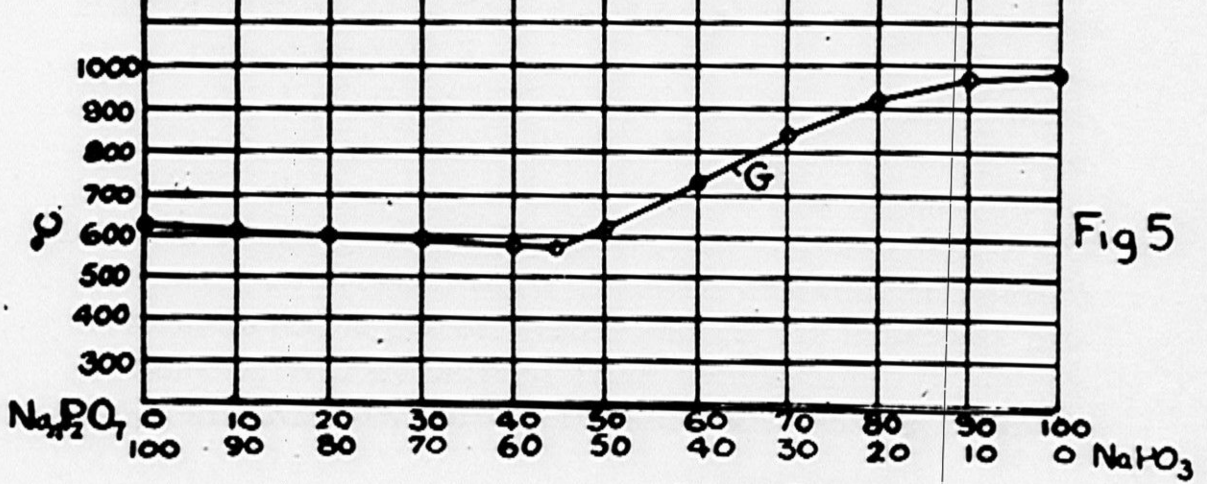

Fig 5

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Allowed Claims

190 62. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein to prevent deposition of said compounds therein, the water soluble fused reaction product of sodium metaphosphate and tetrasodium pyrophosphate to produce when dissolved in water an aqueous solution thereof having a pH between 8 and 10, the weight proportions of sodium metaphosphate and tetrasodium pyrophosphate in said reaction product falling within the range of 50:50 and 20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium meta and tetrasodium pyrophosphate.

191 63. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein, to prevent deposition of said compound, the fused reaction product of monosodium and disodium orthophosphate, to produce when dissolved in water an aqueous solution having a pH between 8 and 10, the weight proportions of $NaPO_3$, derived from said monosodium orthophosphate, and $Na_4P_2O_7$, derived from disodium orthophosphate in said reaction product, falling within the range of 50:50 and 20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.

191 64. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein to prevent deposition of said compound, the fused reaction product of monosodium and disodium orthophosphate, to produce when dissolved in water, an aqueous solution having a pH between 9 and 10, the molecular proportions of $NaPO_3$ derived from monosodium orthophosphate, and $Na_4P_2O_7$ derived from disodium orthophosphate

in said heat reaction product being substantially 1 to 1, said heat reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.

191-192 65. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein to prevent deposition of said compounds, the water soluble fused reaction product of soda ash and orthophosphoric acid, to produce when dissolved in water an aqueous solution thereof having a pH between 8 and 10, the theoretical weight proportion of sodium metaphosphate and tetrasodium pyrophosphate in said reaction product falling within the range of 50:50 and 20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.

192 66. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein to prevent deposition of said compound, the water soluble fused reaction product of soda ash and orthophosphoric acid to produce when dissolved in water an aqueous solution thereof having a pH between 7 and 10, the theoretical weight proportion of sodium metaphosphate and tetrasodium pyrophosphate in said reaction product falling within the range 20:80 and 80:20 respectively, said heat reaction product containing a proportion of sodium acid pyrophosphate, and being characterized further in that its power to prevent deposition of said alkaline earth metal compounds is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.

* * * * * * * * * *

APPELLEE'S EXHIBIT NO. 1.

384 A—Tanner, 123,743

B—Precht, 502,424

C—Hall et al., 1,903,041

D—Hall, 1,956,515

E—Precht, British, 7,958

F—"The Polyphosphates," N. Parravano, G. Calcagni, Zeitschrift Fur Anorganische Chemie, Vol. 65 (1910), pp. 1 to 9.

G—Gmelins Handbuch, 8th Edition, Vol. Sodium (1927), pp. 924-5.

H—Print of Drawings (Not reproduced here. See Appellant's Ex. No. 17 supra),

I—Examiner's Statement,

J—Examiner's Supplementary Statement,

K—Decision of the Board of Appeals,

L—Decision of the Board of Appeals on Request for Correction of Typographical Error,

M—Decision of the Board of Appeals on Request for Amendment of Decision.

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UNITED STATES PATENT OFFICE.

BENJAMIN TANNER, OF NEW BRIGHTON, ENGLAND.

IMPROVEMENT IN THE MANUFACTURE OF PHOSPHATES OF THE ALKALIES.

Specification forming part of Letters Patent No. 123,743, dated February 13, 1872.

I, **Benjamin Tanner**, of New Brighton, in the county of Chester, England, have invented certain "Improvements in the Manufacture of Phosphates of Soda and other Alkaline Bases," of which the following is a specification:

It is a well-known fact, which has been described in standard chemical works published many years since, that acid phosphate of soda may be produced in the following manner: "One atom of phosphoric acid heated with common salt unites with only one atom of soda, and, with two atoms of basic water, forms this salt," namely, acid or monophosphate of soda. From the acid phosphate of soda the other forms of phosphate of soda are obtained by various well-known processes. I have discovered that by the use of the improved processes of manufacture hereinafter described I am able to produce acid phosphate of soda and other forms of phosphate of soda much more efficiently and economically than by any of the processes heretofore known or in use. The employment of chloride of sodium or common salt has been hitherto attended with difficulties, owing to the fact that the temperature which was considered necessary to decompose more than one equivalent of chloride of sodium displaced the basic water, thereby forming pyrophosphate of soda, or mixtures of metaphosphate and pyrophosphate of soda. This necessitated the use by the operator who desired to produce other forms of phosphate of soda of the more expensive sources of soda in the form of caustic soda, or carbonate of soda, or sulphate of soda. By the present invention I am enabled to obviate the difficulties above mentioned by submitting, in the manner hereinafter described, the materials which are employed to the action of steam, superheated steam, or mixtures of steam and hot air, or mixtures thereof, with or without the assistance of heat applied to the bottom of the furnace in which the operation is carried on, whereby the decomposition is accomplished more perfectly and with greater facility, less expensive materials being available for the manufacture, and the difficulty hereinbefore referred to is conveniently overcome. It will be seen that the materials operated upon are those which have been, as is well known, previously used; but the mode of operating upon them, and, in particular, the use of the steam, superheated steam, and hot air, hereinafter described, will, as I have discovered, produce far more beneficial results than could have been obtained by any other process previously discovered with which I have hitherto been acquainted.

For the convenience of reference, the several portions of this specification will be consecutively numbered.

First. For the production of monosodic phosphate (having a composition of one equivalent of soda, two equivalents of basic water, and one equivalent of phosphoric acid, with or without water of crystallization) phosphoric acid is mixed with chloride of sodium in such proportions that one equivalent of phosphoric acid shall react upon one equivalent of chloride of sodium, and for this purpose it is preferred to use seventy-one hundred weights of phosphoric acid with about fifty-eight and a half hundred weights of chloride of sodium. These materials may be used in a more or less pure condition. In practice, they may be mixed in the proportion of three hundred and fifty-five hundred weights of commercial phosphoric acid, containing twenty per cent. of phosphoric acid, and about sixty-five hundred weights of common salt, containing ninety per cent. of chloride of sodium. This operation may be performed in any convenient vessel in which the temperature can be easily raised; but furnaces made of fire-clay, or constructed in a similar manner to those employed in the manufacture of soda-ash, are preferred for this purpose. In order to effect the evaporation of the mixture, I employ currents of steam, or mixtures of steam and hot air, or superheated steam, or mixtures thereof. These currents are made to pass over into or through the mixture or mixtures acted upon, either with or without the employment of additional heat applied to the bottom of the furnace in which the operation is performed, and the heat is continued to be applied until acid fumes cease to be thrown off. When superheated steam is used to effect the required decomposition, the temperature of the steam may safely be raised to 350° or 400° Fahrenheit, and in some cases the temperature may be increased to 450° Fahrenheit without injury to the product obtained. When mixtures of hot air and steam are employed for this purpose, the requisite temperature is regulated according to the proportion in which the steam and hot air are mixed; thus the temperature of the mixture of hot air and steam should be lowered from that above named down to about from 220° to 250° Fahrenheit as the proportion of steam in the mixture is decreased. The above-named materials may be mixed in a reverberatory furnace and treated in the same way as that by which sulphate of soda is commonly made, simply substituting phosphoric acid in the proper proportion (which would be well known) for the sulphuric acid employed in such manufacture, and in making use of the ground heat supplied (which it is preferred should not rise beyond 280° Fahrenheit) in conjunction with mixtures of steam and hot air, or superheated steam, or steam, or mixtures thereof. The temperature should be controlled within the desired limits, as already described. I have found that the use of either superheated steam, or mixtures of hot air and steam, or steam, or mixtures thereof, by passing the same into, over, or through the material, as above described, very much assists the liberation of the acid fumes, (which is usually continued till they cease to be evolved,) and tends to make the decomposition comparatively more rapid and perfect. The fumes thrown off are condensed or utilized by well-known processes, and which form no part of my said invention. The monosodic phosphate produced by either of the foregoing processes is sometimes dissolved by means of water, and may be evaporated or crystallized by any of the methods now employed for such purpose, or purified by other convenient and usual arrangements.

Second. When it is desired to produce bisodic phosphate, (having a composition of two equivalents of soda, one equivalent of basic water, and one equivalent of phosphoric acid, with or without water of crystallization,) the only variation from the processes described in the paragraph hereof numbered 1 which is necessary is an increase in the quantity of chloride of sodium, which, for this purpose, should be added in double the proportion named therein—that is to say, for three hundred and fifty-five hundred weights of commercial phosphoric acid, containing twenty per cent. of phosphoric acid, about one hundred and thirty hundred weights of common salt, containing ninety per cent. of chloride of sodium, would be required. The higher temperature—by the use of steam, or superheated steam, or mixtures of hot air and steam, or mixtures thereof, as described in paragraph hereof numbered 1—is preferred, and when necessary the bisodic phosphate is purified, as hereinbefore described.

Third. When trisodic phosphate (having a composition of three equivalents of soda and one of phosphoric acid, with or without water of crystallization) is required, either of the processes described in the paragraph hereof numbered 1 is adopted, (using, by preference, the higher temperature hereinbefore described,) with an increase in the quantity of common salt, which should be, as nearly as is practicable, three times the quantity named in the last-mentioned paragraph—that is to say, for three hundred and fifty-five hundred weights of commercial phosphoric acid, containing twenty per cent. of phosphoric acid, about one hundred and ninety-five hundred weights of common salt, containing ninety per cent. of chloride of sodium, would be necessary. In some cases, at the stage of the process when acid fumes cease to come off, the product may be subjected to heat gradually increased to a red heat, with or without the continued application of steam, or superheated steam, or mixtures of hot air and steam, or mixtures thereof, in the manner already described, so as to displace any chlorine remaining. The trisodic phosphate obtained by either of the foregoing processes may be purified by the methods of purification ordinarily used, as hereinbefore described. When the phosphoric acid employed in either of the foregoing processes contains any acid capable of decomposing chloride of sodium, (such as sulphuric acid,) either as an impurity or admixture, a larger quantity of chloride of sodium will be required. If the phosphoric acid contained ten per cent. anhydrous sulphuric acid, either as an impurity or admixture, then ten tons of such acid would contain one ton anhydrous sulphuric acid, and would require about thirty-three hundred weights of commercial chloride of sodium of ninety per cent. purity in addition to the quantity required for the phosphoric acid. The sulphate of soda so formed may either be allowed to remain in the product, or be separated by crystallization or by any convenient arrangement.

Fourth. The proportions in which the materials are mixed should, as is well known, be regulated by their purity and strength, and by the condition or form in which it is desired to obtain either of the phosphates of soda; but for economical working it is preferred to use the phosphoric acid in the proportion of one equivalent of phosphoric acid to one, two, or three equivalents of soda, and, by increasing and continuing the temperature in the manner described, monosodic, bisodic, or trisodic phosphate can be efficiently and very economically produced. For the convenience of manufacture, it is preferred to add the required quantity of phosphoric acid and chloride of sodium by one and the same operation; but it is evident that the same end may be attained by successive additions at different stages of the operation, and, also, by regulating the proportion of chloride of sodium employed, mixtures of any of the foregoing phosphates can be obtained. By means of the foregoing treatment, and on the same principle, monosodic or bisodic phosphate, or metaphosphate, or pyrophosphate of soda, or mixtures thereof, can be made to react on chloride of sodium for the production of any of the before-named phosphates of soda by regulating the proportion of the mixture according to the product desired. In some cases it is found advantageous to intermix with the mass, either before or after evaporation, coke or pumice-stone, or some similar material, preferably in small lumps, and then proceed in the manner already described. When the decomposition is completed, the mass may be lixiviated by any suitable arrangement, and the phosphate of soda obtained in the manner described in the paragraph hereof numbered 1. The coke or pumice-stone, or other materials, can be again employed for a similar purpose, or the mixture may be reduced to powder without separation of the coke or pumice-stone. The coke or pumice-stone, or similar materials, so employed divides the mass, and keeps the mixture more open to the action of the steam, or superheated steam, or mixtures of steam and hot air, and thus facilitates the completion of the process.

Fifth. The processes of manufacture above described for producing phosphates of soda are employed in the production of phosphates of other alkaline bases (such as potash or ammonia) by the employment of the chloride of either of the other alkalies, these being treated in the same manner as has been herein described for chloride of sodium, and the proportions in which they are used being varied according to their respective equivalents or combining proportions, which are well known to chemists and recognized in manufacturing processes. In like manner, and on the same principle, phosphates having more than one alkaline base may be produced by using, in the manner herein described, a mixture of the said bases, or of the aforesaid compounds thereof, instead of using a single base or any of the before-mentioned compounds thereof.

It should be observed that the proportions of the substances employed for the purposes of my said invention are not in all cases precisely such as are hereinbefore mentioned, as such proportions may, as will be well known to persons experienced in the manufacture of analogous chemical products, in some instances, be varied without departing from the principles of my said invention.

Having thus described and ascertained the nature of my said invention, and in what manner the same is to be performed, I would observe, in conclusion, that what I consider novel and original, and therefore claim as constituting the invention intended to be secured to me, are—

1. The production of monosodic, bisodic, or trisodic phosphates, or mixtures thereof, by the aid of currents of steam, or superheated steam, or mixtures thereof with heated air, in the manner hereinbefore substantially described and set forth;

2. The production of the corresponding salts of potash or ammonia by the aid of currents of steam, or superheated steam, or mixtures thereof with heated air, in the manner hereinbefore substantially described and set forth; and

3. The production of tribasic phosphates having more than one of the before-mentioned alkalies (namely, soda, potash, or ammonia) as bases thereof, by the aid of currents of steam, or superheated steam, or mixtures thereof with heated air, in the manner hereinbefore substantially described and set forth.

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UNITED STATES PATENT OFFICE.

HEINRICH PRECHT, OF NEU-STASSFURT, GERMANY.

PROCESS OF OBTAINING META OR PYRO PHOSPHORIC-ACID COMBINATIONS.

SPECIFICATION forming part of Letters Patent No. 502,424, dated August 1, 1893.

Application filed June 16, 1892. Serial No. 436,945. (No specimens.)

To all whom it may concern:

Be it known that I, HEINRICH PRECHT, a subject of the King of Prussia, residing at Neu-Stassfurt, Prussia, Germany, have invented certain new and useful Improvements in and Relating to the Production of Phosphate of Potassium and of Alumina; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

My invention relates to the production of phosphate of potassium and of aluminum.

It is well known that the meta phosphate of potassium heretofore produced is insoluble in water or substantially so, and my invention has for its object a process whereby phosphates of potassium and of aluminum readily, in fact, completely soluble in water may be readily obtained by conversion of the insoluble into soluble salts, in which all of the contained phosphoric acid is in a form readily soluble in water. This I attain as hereinafter more specifically described by subjecting the potassium meta phosphate to a melting process, and if this process is carried out in such manner that the meta phosphate is rapidly cooled, that is to say in such a manner as to prevent crystallization, an amorphous potassium salt of the concentrated metaphosphate that is readily soluble is obtained. The potassium meta-phosphate may be obtained in any well-known manner, as for instance by heating potassium mono-phosphate (KH_2PO_4), or by melting, preferably by means of steam, potassium carbonate or potassium chlorid together with metaphosphoric acid in such proportions that the compound will contain one atom of P for each atom of K.

In carrying out my invention I proceed as follows: The insoluble potassium metaphosphate is melted and then allowed to flow into a shallow flat iron vessel or into shallow channels for the purpose of rapidly congealing the same so that it will not crystallize but remain in an amorphous condition. A potassium salt of the concentrated metaphosphate is thus formed which by slow cooling would revert into a crystalline and insoluble compound.

The melting of the insoluble potassium metaphosphate can be effected with the best advantage in a reverberatory furnace in which the phosphate is heated to such a degree as to render it fluid so that it may be allowed to flow out of a tap-hole. If the melting is effected in a reverberatory furnace provided with an inclined sole or hearth the operation can be made a continuous one by feeding the phosphate into the furnace at the highest and coolest point of the hearth, which should incline toward the source of heat, and allowing the molten material to flow from a tap-hole at the lowest and hottest point of such hearth, and if necessary the material may be raked down the incline so that the salt will be gradually reduced to a fluid state. The melting of the phosphate is advantageously effected by subjecting it to the action of an oxidizing flame as a reducing flame might result in a reduction of the phosphoric acid, which would be detrimental.

Practical experience has demonstrated that a potassium phosphate completely soluble in water is obtained when the molten mass contains one molecule of phosphoric acid (P_2O_5) to one molecule of potassium oxid (K_2O) or one hundred parts by weight of anhydrous phosphoric acid, (P_2O_5) or phosphoric acid free from water, to at least 66.2 parts by weight of potassium oxid (K_2O). In practice it will, however, be found of advantage to operate with a larger proportion of potassium oxid (K_2O) so that phosphoric acid in the form of pyrophosphate will in part be present in the molten salt. If the proportion of potassium oxid (K_2O) relatively to the phosphoric acid is such that one part of potassium pyrophosphate to four parts of potassium metaphosphate must be formed in the molten mass, potassium metaphosphate that is completely soluble in water is readily obtained, as above described. In order that these proportions may be obtained a basic body, such as potash or soda, the quantity of which will correspond to the desired combination or composition, is added to the potassium metaphosphate either before or during the melting of the same.

The soluble potassium phosphates obtained as above described can be employed in the production of soluble phosphate of alumina or of orthophosphate of potassium soluble in water as follows: In the production of phosphate of alumina soluble in water, the phosphate of alumina is mixed with the soluble potassium metaphosphate or potassium pyrophosphate or both, obtained as hereinbefore set forth, in any desired proportion within the limit of forty per cent. of phosphate of alumina, the soluble potassium meta or pyro phosphate forming with the phosphate of alumina combinations that are soluble in water and whose solutions do not decompose. The phosphate of alumina, as such and in its insoluble form, is added to the potassium meta or pyrophosphate or to a mixture of them, either during the process of melting or to the potassium phosphates in the phosphoric acid solution employed as a starting material, in that a solution of phosphoric acid contaminated with or rendered impure by alumina is employed in the production of the insoluble phosphates. Should the phosphate of alumina contain a small proportion of iron the latter is also converted into a soluble form.

In the production of potassium orthophosphate from the soluble meta or pyrophosphates of potassium or of a mixture of them, the latter salts are dissolved in water until the solution is of a specific gravity of about 1.25, which solution is then heated under pressure in a closed vessel by means of steam, to a temperature a little above the boiling point. The higher the temperature within certain limits the more rapidly will the conversion take place, said conversion being completed in about two hours at a temperature of about 120° centigrade, the reaction being somewhat accelerated by addition of phosphoric acid to the solution.

The products obtained by my invention may be used for any purposes in the arts and manufactures, but are particularly applicable for use as fertilizers in that they contain potassium oxid and phosphoric acid and are therefore well adapted as substitutes for that class of fertilizers which contain chemical combinations of potassium together with phosphatic constituents, and have the advantage over the latter fertilizers in that said products do not contain undesirable chlorids.

Having thus described my invention, what I claim as new therein, and desire to secure by Letters Patent, is—

1. The herein-described process of obtaining meta or pyro-phosphoric acid combinations from phosphate salts of the metals of the alkalies, which consists in melting the insoluble salt or salts and rapidly cooling the same to prevent crystallization for the purpose set forth.

2. The herein-described process of obtaining meta or pyro-phosphoric acid combinations, from phosphate salts of the metals of the alkalies, which consists in melting the insoluble salt together with a salt of the metals of the alkalies, and rapidly cooling the same to prevent crystallization for the purpose set forth.

HEINRICH PRECHT.

Witnesses:

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Patented Mar. 28, 1933 **1,903,041**

UNITED STATES PATENT OFFICE

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WATER TREATMENT

No Drawing. Application filed November 23, 1929. Serial No. 409,416.

The present invention relates to water treatment, and particularly to the treatment of steam boiler water, and more especially to the treatment of the steam boiler water by chemicals whose aqueous solutions are either alkaline or of relatively slight acidity, but which through changes wrought in their character at the temperatures and under the conditions obtaining in the boiler water undergo transformation which increases their alkali-neutralizing capacity. The solutions of the treating chemicals, which may be either alkaline or of relatively slight acidity, can be handled with little if any corrosive attack upon the supplying or injecting devices.

In its more specific embodiment, the invention relates to the use of treating chemicals which, in addition to being transformed in the boiler water into substances with greater alkali-neutralizing capacity, supply radicals, after the transformation, which will combine in the boiler water with the scale-forming alkaline-earth metals to form non-adherent sludge, and thereby prevent the formation of adherent boiler scale.

The specific and preferred chemicals having these properties are the metaphosphates and pyrophosphates which are transformed by chemical change in the highly heated boiler water with relative rapidity into acid orthophosphates yielding orthophosphate radical which maintains the equilibrium in the boiler water necessary for the prevention of scale, and acid hydrogen which counteracts the tendency to excessive concentration of alkalinity in the boiler water.

Treating chemicals, such as the metaphosphates and pyrophosphates, cause or permit to be maintained the necessary alkalinity of the feed water to prevent corrosive attack upon the feed water heaters and lines. The calcium metaphosphates and the calcium pyrophosphates are considerably more soluble than tricalcic orthophosphate. Hence, the addition of the metaphosphate and pyrophosphate to the feed water is much less productive of supersaturation of insoluble calcium salts therein and hence less productive of any tendency to form feed line deposits.

In modern steam generating practice, every effort is made for efficiency, both from the standpoint of conserving fuel and from that of deriving most steam from each generating unit. In order to obtain the desired efficiency it is essential that all surfaces of the steam-generating system making contact with water be protected from deterioration, whether such deterioration consist in formation of scale thereon, or impairment thereof by corrosion, corrosion fatigue, or the effects sometimes described as "embrittlement", and that those conditions be established and continuously maintained in the boiler water which are best adapted to minimizing any entrainment thereof in the effluent steam.

We will define first conditions in the contacting water that best prevent dissolution of the retaining iron or steel surfaces, whether this dissolution be general over the surfaces or manifest itself in form of pits or grooves.

From all standpoints it is best that content of dissolved oxygen in the water be made as small as possible, and more especially beginning with the point in the system at which the temperature is raised above ordinary room or outside temperature. Inasmuch as this factor in preventing corrosion is not of specific application in this specfication, we will assume in the following discussion that provision is made for satisfactory deaeration of the water.

It has been established that a slight alkalinity in water making contact with iron or steel best prevents corrosion. The pH value of a sample drawn from any point of the system should be in no case less than 8, (the determination is made by any of the usual methods after the sample is cooled to approximately room temperature) and is better maintained somewhat higher than this. Thus, in the feed water heater, feed lines and economizer, a pH value of the water of 8, while largely minimizing any corrosion, is not as effective therefor as a pH value of between 9 and 10. In the boiler water proper, the pH value (determined as described above) should never be below 10, and is best maintained slightly higher, approximately 11.0 to 11.5 in a great number of cases.

If the feed water is softened by one of the various types of lime-soda softener, with correct operation, its pH value in general will lie within the limits specified above for heater, feed lines and economizer, and thus is not corrosive thereto. Admixture of pure return condensate with the softened water, by dilution of the latter, lowers its pH value, and in case of high percentage of condensate, may reduce it below the desirable point, so that increment thereto by addition of solution of appropriate alkaline chemical may be advisable. The boiler water, however, integrates this slight alkalinity of the feed water into higher alkalinity in itself—the alkalinty does not pass out of the boiler with the steam—and in inverse proportion to the blowdown. Conservation in blowdown is one factor in obtaining efficiency of operation, but because the boiler water represents a summation of, and therefore contains many times the alkalinity of the feed water, limitation of the boiler-water alkalinity to the desirable concentration must frequently be obtained, either by greater blowdown than necessary for other purposes, by maintenance of less alkalinity in the feed water than desirable, by introduction of an acid ingredient directly to the boiler water with all the operating difficulties incident thereto, or by other means.

It is extremely important that the boiler water be maintained alkaline, but that the alkaline concentration be confined rather closely to a pH value of over about 10, but not over about 11.5. The boiler water should be alkaline to this extent, because this condition best obviates any tendency of the boiler metal to dissolve or to pit, and also gives best and most economical use of the conditioning chemical. But it should exceed this limit as little as possible because of the tendency of increasing alkalinity to originate or augment carry-over of boiler water in the steam and because of its inimical effect on the boiler metal, especially if it concentrates in seams or around rivets, because by its cleansing or peptizing effect, or at higher concentrations, its ability actually to cause dissolution of the metal or protective films integral therewith, it may be accelerative of corrosion-fatigue or "embrittlement", and hence rupture of the boiler metal.

With use of natural untreated water as make-up, or of water treated in a zeolite softener, the difficulties are increased. Many, in fact, most natural waters, contain bicarbonate associated with calcium and/or magnesium and/or alkali metal as sodium. In the zeolite softener, sodium is substituted for the calcium and/or the magnesium, and in the boiler, sodium bicarbonate decomposes to form first sodium carbonate, which in turn, largely suffers decomposition into caustic soda.

In this manner, tremendous alkalinity may be developed in the boiler water. At the same time, the pH value of the feed water may be insufficient to prevent corrosion of the feed water lines and pumps unless alkali is added thereto. If natural water is treated by trisodium phosphate, the same development of sodium bicarbonate and finally of sodium hydroxide in the boiler water occurs, but its use has the advantage of increasing the pH value of the feed water. Usually the development of excessive alkalinity in the boiler water occurs as the result of using pretreatment of the feed water, either by the zeolite process or by the lime soda process, or by direct treatment with the alkali-metal orthophosphates or carbonates. However, there are natural waters which contain alkali-metal bicarconate, and these without treatment, if used for boiler feed, will develop high alkalinity in the boiler water.

For protection of the boiler metal from "embrittlement", it is considered advisable by many (as in Suggested rules for care of power boilers, Section VII (1927) paragraph CA—5, The American Society of Mechanical Engineers), that the content of sodium sulphate in the boiler water bear continuously to the total alkalinity therein a ratio which is definite for any operating pressure, but which increases with increase of operating pressure. Thus, if a minimal value of the alkalinity in the boiler water is not assured, maintenance of these ratios engenders difficulties in two ways, namely:

1. Large quantities of sodium sulphate must be maintained in the boiler water, and particularly at higher operating pressures where it is least desirable, thus, on the one hand occasioning difficulty by reason of bad boiling conditions and concomitant poor quality of steam, endangering continuity of operation through failure of superheater tubes, or damage to prime movers; or on the other hand, requiring unnecessarily large blowdown to obviate these difficulties. Furthermore, under these circumstances, it is frequently necessary to augment the sodium sulphate present in the natural water by its addition thereto, and thus needless increase of cost of water conditioning is incurred.

2. The large amount of sodium sulphate in the boiler water greatly augments possibilities of scale formation and thus endangers continuity of operation.

Maintenance of the recommended ratios of sodium sulphate to total alkalinity in the boiler water renders well nigh impossible cleanliness of surface essential in high-pressure or high-rating boilers, whether the feed water consist of return condensate, evaporated water, lime-soda or zeolite treated water, unless there be maintained continuously in the boiler water available in solution those concentrations of some stable radical as orthophosphate requisite to govern the character of any solid phase that forms, and thereby insure its formation as non-adherent sludge. In condensate returns and evaporated water, calcium is practically invariably present, due, respectively, to in-leakage of cooling water and carry-over.

Effluent water from the lime-soda softener even when it is operated most efficiently, contains sufficient calcium so that its accumulation in the boiler water, in conjunction with the sodium sulphate required for protection from "embrittlement", results in exceeding the solubility-product relations of calcium and sulphate at pressures above about 160 pounds, and hence, in scale deposition. While the calcium content of water from a carefully operated zeolite softener in good condition is usually less than that from the lime-soda softener, possibility of scale formation is lessened but not obviated, and certainty of scale prevention with a zeolite-softened water, as well as with all others, abides in the maintenance of essential conditions in the boiler water, as described in United States Patents Nos. 1,613,656 and 1,613,701, issued to Ralph E. Hall on January 11, 1927. Presence of a stable radical as orthophosphate available in solution in the boiler water. becomes particularly necessary in view of higher pressures and ratings, and the desirable small, closely controlled alkalinities in the boiler water that characterize present steam-generating practice.

Use of disodium or monosodium phosphate in the feed water is effective in decreasing the total alkalinity developed in the boiler water, but has little effect on or is inimical to the maintenance of desired pH values in the feed water.

These difficulties may be met by addition of acid to the feed water to destroy its bicarbonate, removal of the dissolved carbon dioxide by satisfactory means, and subsequent addition of alkalinity by means of an alkaline chemical, as trisodium phosphate, in amount sufficient to develop the desired pH value in the feed water; or by means of returning continuous blowdown from the boiler at appropriate point to the feed water, so that the boiler-water alkalinity is made use of in developing the desirable pH value in the feed water. (This is practically without value when the pH value of the boiler water is maintained between 10 and approximately 11). These methods are relatively complex and costly, and require very careful control.

There is, therefore, a distinctly difficult problem presented by the necessity of maintaining an alkaline condition in the feed water, and yet limiting concentration of alkalinity in the boiler water to that compatible with safe or desirable operating conditions, and at the same time continuously maintaining in the boiler water a sufficient concentration of a radical, such as orthophosphate, to insure the precipitation of calcium and/or magnesium as non-adherent sludge instead of adherent scale.

The solubility of tricalcic phosphate is very slight, and addition of orthophosphate radical to the feed water very frequently occasions supersaturation therein with respect to tricalcic phosphate. This supersaturation is not immediately completely relieved by separation of solid phase, but persists, with the result that solid phase continues to separate along the path of the feed water to the boiler, and particularly at points tending to destroy the condition of supersaturation, as where the temperature of the feed water is considerably raised, as in an economizer or a heater fed with steam bled from one of the stages of the turbine. Separation of solid phase under these conditions occurs in part at least as scale, adherent to feed lines, feed water pumps, heaters, economizers, etc., and at times in desuperheating equipment.

A solution of these various difficulties lies in derivation of the essential phosphate or other conditioning-chemical concentrations in the boiler water by addition to the feed water of conditioning chemicals whose calcium compounds are relatively soluble, and which are either alkaline of reaction themselves when dissolved in water, or offer no difficulties to maintenance of the desired pH value in the feed water, but which, when subjected for a period to higher temperature as that of the boiler water, provide the necessary orthophosphate or other conditioning radical therein, and simultaneously neutralize part of the boiler-water alkalinity.

As one example, alkali-metal pyrophosphates and metaphosphates meet these requirements. Thus, if sodium pyrophosphate ($Na_4P_2O_7$) is heated with water at sufficient temperature, the folowing reaction occurs:

$$(1)\quad Na_4P_2O_7 + H_2O \rightarrow 2Na_2HPO_4$$

If sodium metaphosphate ($NaPO_3$) (or a polymerized form thereof) is so heated, the reaction is as follows:

$$(2)\quad NaPO_3 + H_2O \rightarrow NaH_2PO_4$$

If for any reason addition of acid to the feed water be advisable, then use of the acid alkali-metal pyrophosphate salts or of metaphosphoric or pyrophosphoric acids is advantageous, both from the standpoint of the relatively large solubility of calcium metaphosphate or pyrophosphate, thus averting feed line deposits, and the increased neutralization of alkalinity that is obtained in the boiler water because of the transformation of these substances to acid orthophosphates at boiler water temperatures. The transformations that occur may be represented as folows:

(3) $Na_2H_2P_2O_7+H_2O \rightarrow 2NaH_2PO_4$
(4) $H_4P_2O_7+H_2O \rightarrow 2H_3PO_4$
(5) $HPO_3+H_2O \rightarrow H_3PO_4$

Reactions (2) and (5) may occur in steps thus:

(6) $2NaPO_3+H_2O \rightarrow Na_2H_2P_2O_7$
$2HPO_3+H_2O \rightarrow H_4P_2O_7$

the further change to orthophosphate occurring in accordance with reactions (3) and (4).

The above equations show that addition of a pyrophosphate or a metaphosphate in appropriate amounts to the feed water will result in the maintenance of desired quantities of orthophosphate radical in the boiler water. These reactions are hastened by the temperature of the boiler water and by the continuous removal therefrom of the end product, namely, orthophosphate, by any incoming calcium, thus minimizing the establishment of any equilibrium in the reaction.

The pyrophosphoric acid and metaphosphoric acid may be prepared by heating orthophosphoric acid. Upon heating the orthophosphoric acid (H_3PO_4), to appropriate temperature, water is driven off, producing pyrophosphoric acid ($H_4P_2O_7$). Upon heating, two molecules of orthophosphoric acid produce one molecule of pyrophosphoric acid, as follows: $2H_3PO_4=H_4P_2O_7+H_2O$. The loss of the water causes a rearrangement of the atoms within the acid molecule with the result that the pyrophosphoric acid produced has less alkali-neutralizing capacity than the orthophosphoric acid from which it was produced. Upon heating to appropriately higher temperature, more water is driven off and the pyrophosphoric acid is transformed into metaphosphoric acid (HPO_3), which has still less alkali-neutralizing capacity than the pyrophosphoric acid from which it was produced, due to a still further atomic rearrangement. Both the pyrophosphoric acid and the metaphosphoric acid may be neutralized by alkali-metal hydroxide, such as sodium hydroxide, yielding alkali-metal pyrophosphate or alkali-metal metaphosphate.

Likewise, by heating at appropriate temperatures, acid orthophosphate salts may be converted into pyro- or metaphosphate salts. The terms "pyrophosphate" and "metaphosphate" when used without other qualification are intended to include pyrophosphoric acid and metaphosphoric acid, as well as the salts of these acids, since pyrophosphoric acid and metaphosphoric acid may be considered as hydrogen pyrophosphate and hydrogen metaphosphate. Similarly, by the term "molecularly dehydrated phosphate" we intend to include the acids as well as the salts.

The water solutions of pyrophosphoric acid and metaphosphoric acid or salts thereof tend to revert to the orthophosphate form, the speed of reversion depending upon the attendant circumstances. The reversion is relatively slow at normal room temperatures and particularly in dilute alkaline solutions. The reversion, however, is accelerated by the high temperature of the boiler water and the removal of the orthophosphate end-product by the calcium in the boiler water. The reversion from the meta- or pyro-condition to the ortho-condition is relatively slow in the feed lines where the temperature is lower, but rapid in the boiler where the temperature is higher.

The reversion is due to the recombination of water with the pyro- or metaphosphate. By such rehydration, sodium pyrophosphate which has an alkaline reaction, is converted into disodium monohydrogen orthophosphate whose hydrogen is an acid hydrogen and is therefore capable of neutralizing alkalinity. Similarly, sodium metaphosphate, the solution of which is very slightly acid, is transformed into monosodium dihydrogen orthophosphate, which has twice the alkali-neutralizing power of disodium monohydrogen orthophosphate. Similarly, pyrophosphoric acid and metaphosphoric acid may be converted by rehydration into orthophosphoric acid with an increase in alkali-neutralizing capacity. The conversion into the more acid condition is what may be termed a molecular rehydration, in that the water goes into chemical combination with the metaphosphate or pyrophosphate radical, causing an atomic rearrangement of the atoms of the molecule, as distinguished from the absorption of water of crystallization by solid phase which does not effect a rearrangement of the atomic linking within the molecule; and as distinguished from the hydrolysis of a salt dissolved in water, as, for instance, alkali metal alum or bismuth chloride dissolved in water.

The pyro- and meta-salts and acids may be considered as molecularly dehydrated forms of the ortho-salts and acids, since the dehydration effects an atomic rearrangement within the phosphate molecule, as distinguished from the so-called dehydration of orthophosphates by heating merely to drive off water of crystallization, or the double-decomposition reactions characterizing hydrolysis. Therefore, for convenience, we employ the expression "molecularly dehydrated" to distinguish as a class the pyro- and meta-salts and acids from the ortho-salts and acids. Thus, for example, by the expression "molecularly dehydrated phosphate", we mean the pyro- or metaphosphate as distinguished from an orthophosphate from which merely water of crystallization has been driven off and which is sometimes referred to as "dehydrated" or "anhydrous" salt, and by a "molecularly dehydrated phosphate radical" we mean to include pyrophosphate radical (P_2O_7) or meta-phosphate radical (PO_3), one or the other of which is formed in the molecular dehydration or driving off of water from the orthophosphate acid or acid salts. The expression "phosphate" when used alone in the claims is intended as a term of general definition and not of limitation, and to include the orthophosphate, pyrophosphate and metaphosphate, unless one of such types of phosphate be specifically specified. Similary, the expression "arsenate" is intended to include the orthoarsenate, pyroarsenate and metarsenate, unless one of such types of arsenate be specifically specified.

The alkali-metal normal salts of the pyrophosphates, when dissolved, give a pH value higher than that of pure water, those of the metaphosphates give a pH value practically the same or slightly less than that of pure water. And yet, as shown by the above reactions, their addition to the feed water results not in increased, but decreased alkalinity in the boiler water, since in the transformation into orthophosphate the pyrophosphate molecule supplies two molecules of disodium phosphate (Na_2HPO_4), the hydrogen of which is an acid hydrogen, and will neutralize its equivalent of alkalinity. Likewise, the metaphosphate molecule supplies one molecule of monosodium phosphate (NaH_2PO_4), whose two hydrogen atoms are acid hydrogen, and will likewise neutralize their equivalents of alkalinity. Likewise, use of pyro- or metaphosphoric acid as conditioning chemical results in greater neutralization of alkalinity in the boiler water than corresponds to the alkali-neutralizing capacity of the acids introduced.

Finally, the calcium salts of the pyrophosphates and the metaphosphates are much more soluble than tricalcic phosphate, and hence, the condition of supersaturation that so readily obtains upon addition of orthophosphate to the feed water occurs not at all or in very much less degree with addition of pyrophosphates or metaphosphates, thus preventing or minimizing the tendency to deposit scale in the feed water lines and heaters.

The solubility of the calcium salts of the pyrophosphates and the metaphosphates is high enough so that deposition thereof in feed-water heaters or feed-water lines is not liable to occur, unless considerable change of the pyrophosphate or metaphosphate into orthophosphate occurs therein. This change is a time reaction which will take place in heated alkaline solutions of the pyrophosphates and metaphosphates. Thus, if the system includes an economizer there is a tendency for some formation of scale therein due to the conversion of the calcium pyrophosphates or metaphosphates into calcium orthophosphates, which is difficultly soluble and which may be precipitated from a supersaturated solution thereof onto the walls of the economizer or water lines from the economizer to the boiler. If such tendency to the formation of a supersaturated solution of calcium orthophosphate is encountered, it may be counteracted by the addition to the feed water of one or two pounds per million pounds of feed water of cutch, quebracho extract, or similar tannin body. These tannin bodies apparently have the double function of retarding the rate of transformation of pyrophosphate or metaphosphate to orthophosphate, and of stabilizing a supersaturated solution of the orthophosphate, thus serving to inhibit the deposition of scale in the feed water heaters and lines.

Bodies other than the tannin bodies may be used as inhibitors to prevent the deposition of scale in the feed water heater and lines. Other inhibitors are the citrates, such as sodium citrate, lactates, gallates, alginates and gelatine. These inhibitors are, in general, organic bodies having large molecules which apparently both retard the rate of transformation of the pyrophosphate and metaphosphate to orthophosphate and serve to stabilize the supersaturated solution of the calcium orthophosphate. The addition of such inhibitors to feed water containing orthopshosphate for stabilizing the supersaturated condition which may obtain in the feed lines is described and claimed in the copending application of Ralph E. Hall, one of the present applicants, Serial No. 409,417, filed of even date herewith. In the present case, the tannin bodies serve not only to stabilize the supersaturated condition of the feed water, as described in said copending Hall application, but in addition serve to retard the rate of transformation of pyrophosphate or metaphosphate to orthophosphate.

As described above, when the pyrophosphates or metaphosphates are carried by the feed water into the boiler and are there subjected to the continuing high temperature of the boiler water, the pyrophosphates and metaphosphates are transformed into acid orthophosphates, yielding not only acid hydrogen to neutralize excess alkalinity in the boiler water, but also furnishing orthophosphate radical, which serves to maintain the necessary equilibrium in the boiler water to prevent formation of adherent scale.

The necessary equilibrium conditions in the boiler water to prevent the formation of adherent scale are described in the Hall Patents, Nos. 1,613,656 and 1,613,701 of January 11, 1927. As described in said Hall patents, and especially in Patent No. 1,613,656, and with specific reference to the treatment with phosphate of boiler water containing calicum and sulphate, there should be maintained in the water in the boiler a concentration of orthophosphate ion not less than the concentration of sulphate ion to the three-halves power times the ratio of the solubility product of calcium phosphate to the one-half power to the solubility product of calcium sulphate to the three-halves power at the temperature of the water in the boiler, together with proper hydroxide concentration. When such a condition is maintained, the calcium is precipitated as tricalcic phosphate, which is a non-adherent sludge and which can be removed by blowdown, instead of calcium sulphate, which would form adherent anhydrite scale. In other words, in accordance with the Hall patents, there is maintained in the water in the boiler a sufficient concentration of orthophosphate to insure the precipitation of the calcium as non-adherent tricalcic sludge instead of the calcium sulphate scale. The proper tests for the relative concentration of phosphate and sulphate in the boiler water and directions for maintaining the necessary predominance of phosphate in the boiler water, are set forth in detail in said Hall patents and need not be repeated here, and reference may be had to said patents for such details.

The amounts of pyrophosphate or metaphosphate necessary to yield in the boiler water the requisite amount of available orthophosphate radical to insure the precipitation of the calcium and/or magnesium as non-adherent sludge instead of adherent scale, can be readily determined by testing the boiler water for phosphate and sulphate, as described in said Hall patents.

As an example in the use of these conditioning chemicals, consider a water containing 0.6 equivalents per million (30 parts per million) of temporary hardness and 0.2 equivalents per million (10 p. p. m.) of permanent hardness, both expressed in terms of $CaCO_3$. Sulphate concentration in the water is 12 parts per million. Let make-up be taken as 100%, blowdown as 2%, operating pressure as 400 pounds. No preliminary treatment is given the water other than possibly filtration for clarification. Under these conditions, 50 p. p. m. of available PO_4 in solution in the boiler water is sufficient. Conditioning this water completely with sodium metaphosphate dissolved in a convenient amount of water and fed directly at feed-water heater or other convenient point requires 28.3 pounds, approximately, of the anhydrous metaphosphate chemical per million pounds of the feed water. In order that the pH value of the feed water may be that required from the standpoint of preventing corrosion, 0.4 pounds of caustic soda may be added to the 28.3 pounds of metaphosphate.

The solubility of the calcium salt of the metaphosphate is high enough so that deposition thereof in the feed-water heater and feed lines is not likely to occur, unless considerable change from metaphosphate to orthophosphate occurs therein.

But if the system includes an economizer and there is a tendency for some formation of scale therein, then simultaneous introduction with the metaphosphate of one or two pounds per million pounds of feed-water of cutch, quebracho extract, or similar tannin body, will stabilize the supersaturated condition and will retard the rate of transformation from metaphosphate to orthophosphate, so that deposition of scale will not occur.

In the boiler water, with a blowdown of 2%, the sulphate concentration is 600 parts per million. The alkalinity of the boiler water, if the water were treated with trisodium phosphate instead of sodium metaphosphate, would be 30.5 equivalents per million, (1617 p. p. m. expressed as sodium carbonate). But the metaphosphate, by its transformation into orthophosphate, has developed 27.75 equivalents per million of acidity, (sufficient to neutralize 1470 p. p. m. of sodium carbonate alkalinity). Thus the boiler water actually contains 2.75 eq. p. m. of alkalinity, corresponding to 147 p. p. m. total alkalinity calculated as sodium carbonate. The 600 p. p. m. of sulphate corresponds to 888 p. p. m. of sodium sulphate. The ratio of sodium sulphate to total alkalinity as sodium carbonate is 6, which is well above that recommended or proposed by the A. S. M. E. boiler code as protective from damage by "embrittlement".

This example serves to emphasize the fact that the simplest and best protection from the dangers of boiler-metal rupture is obtained by maintaining in the boiler water only the carefully defined minimum alkalinities that are essential from the standpoint of corrosion and economic use of the conditioning chemical.

In the case of pretreatment by zeolite, or direct treatment by trisodium phosphate, the impossibility of maintaining the desired sodium sulphate-alkalinity ratios without neutralization of a large part of the alkalinity developed in the boiler water is apparent from the fact that without such neutralization, sodium sulphate would have to be added to the feed water in sufficient quantity to yield 30×30×53=4770 parts per million of sodium sulphate in the boiler water. With such concentrations of alkali and sodium sulphate in the boiler water, it is doubtful if all possible precautionary measures would avail in preventing carry-over of boiler water with the steam, at the ratings characteristic in modern practice.

The boiler-water alkalinity may be readily reduced still further. Thus, if 29 pounds of the sodium metaphosphote were used per million pounds of feed water, the boiler-water alkalinity would be 2.1 equivalents per million, or 111 parts per million of sodium carbonate. The concentration of available orthophosphate radical would then be 84 p. p. m.

If less alkali-neutralizing capacity is necessary in the boiler water, an alkali-metal pyrophosphate may be used in place of the alkali-metal metaphosphate, or more caustic soda or other alkaline chemical may be used therewith; if more alkali-neutralizing capacity is necessary, metaphosphoric acid or a mixture thereof with the alkali metal metaphosphate may be used.

In general, it is preferable for the boiler plant to maintain a stock of the treating phosphate in one form, for example, sodium metaphosphate. The sodium metaphosphate is very slightly acid in solution. If the raw water is somewhat alkaline or if the water from the primary treatment has sufficient alkalinity, sodium metaphosphate may be used alone for the secondary treatment. On the other hand, if the use of the sodium metaphosphate alone would cause too much acidity, it may be tempered by the addition of a suitable amount of some alkaline reagent, such as caustic soda.

While in the specific example cited above, the treatment was described as applied to a natural water, our treatment may be applied with particular advantage to boiler feed waters which have already undergone a primary treatment, such as the usual lime-soda ash treatment, or zeolite treatment, etc.

To carry out the lime-soda ash process most efficiently, some excess of the treating chemicals is required, which results in excess alkalinity in the treated water. By very careful proportioning of the treating chemicals, the alkalinity can be kept down, but it is advantageous for the efficiency of the process to use a sufficient excess of the treating chemicals which will result in an undesirably high alkalinity in the water if it were to be supplied to the boiler without partial neutralization. The use of the metaphosphates or pyrophosphates may, therefore, be applied with special advantage as a secondary treatment following the lime-soda ash primary treatment, in that the lime-soda ash treatment can be made more efficient, and the increased alkalinity which would result in too great alkalinity in the boiler can be counteracted therein by the acid hydrogen furnished by the rehydration in the boiler of the metaphosphate or pyrophosphate; and this is accomplished without destroying the desirable properties of the alkalinity resulting from the lime-soda ash treatment in preventing corrosion of the feed lines. In the continuous addition of the meta- or pyrophosphate in suitable proportion to the feed water, a relatively steady concentration of alkalinity obtains in the boiler water; we may say, however, that the alkalinity of the boiler water is decreased by such addition of the meta- or pyrophosphate in the sense that the rehydration of the meta- or pyrophosphate steadily furnishes acid hydrogen that neutralizes alkalinity which would otherwise concentrate in the boiler water.

The secondary treatment with the metaphosphate or pyrophosphate also supplements the partial removal of the calcium by the lime-soda ash treatment and precipitates such of the calcium as passes the lime-soda ash treatment to the boiler as a non-adherent orthophosphate sludge in the boiler, thus preventing the formation of scale by the residual calcium from the lime-soda ash treatment.

The zeolite treatment of the raw water, while removing in great part the calcium and magnesium therefrom, nevertheless leaves bicarbonate therein in the form of sodium bicarbonate which, in the boiler water, becomes caustic soda in large measure. The use of the treating chemicals as herein described, therefore, effectively supplements the zeolite treatment and obviates one of its particular disadvantages, namely, that of alkalinity concentration in the boiler from a zeolite-treated bicarbonate water. The acid hydrogen released by the rehydration of the metaphosphate or pyrophosphate counteracts this tendency for alkaline concentration in the water and at the same time, the orthophosphate developed in the rehydration takes care of the residual calcium not removed by the zeolite treatment.

Another advantage is realized in the use of the metaphosphates or pyrophosphates in boiler-water treatment, because of the relatively large solubility of their alkaline-earth metal salts. Thus, in their use for treatment of water for locomotive boilers, their addition to the wayside tank or to the tender of the locomotive produces no precipitation of sludge, with or without pretreatment as by lime-soda or zeolite, and therefore avoids all fouling of valves and supply lines. In the heated boiler water, rehydration of the meta- or pyro- to orthophosphate occurs, thus providing the essential conditions to prevent scale formation and at the same time providing simple control of the alkalinity concentration in the boiler water. Thus, their use, either directly or in conjunction with pretreatment by any of the water softening processes, combines all the advantages of clarity of feed water with full conditioning of the boiler water.

Thus, use of these materials that acquire alkali-neutralizing properties by transformations they undergo in the boiler water is extremely advantageous in that it permits ready maintenance of the desirable low alkalinities in the boiler water, without engendering difficulties from corrosion of the feed lines or the formation of deposits in the feed lines.

As a summary of advantages accruing in conditioning water for boilers from use of conditioning chemicals that undergo desirable transformations in the boiler water as already described, the following among others may be enumerated:

(1) Elimination or minimization of deposits in feed lines, economizers, heaters, desuperheatering equipment, etc., or in the wayside tanks or locomotive tenders.

(2) Possibility of maintenance of desirable pH values in the feed water to prevent corrosion without accumulation of alkalinity beyond desirable proportions in the boiler water.

(3) In most instances, complete elimination of the costly methods of directly feeding acid to the feed or boiler water and the exacting accuracy of control incident thereto, in an effort to maintain desirable concentration of alkalinity in the boiler water. In case, however, the alkalinity to be neutralized is enough so that acid must be used, then use of an acid, such as metaphosphoric, permits very dilute concentration thereof in feed water, since transformation in the boiler water increases the acidity—threefold in the case of metaphosphoric acid. This is of great advantage.

(4) Maintenance of scale-free boilers and simultaneously of the definite slight alkalinity in the boiler water that is essential in modern steam-generating practice. This is essential because—

(*a*) It minimizes any foaming tendency of the boiler water, and hence danger of carryover in the steam.

(*b*) It simplifies the maintenance of sodium-sulphate-alkalinity ratios that are generally believed to be preventive of "embrittlement", and thus obviates largely or entirely addition of sodium sulphate beyond that in the natural water.

(*c*) It necessitates the least blowdown of the boiler.

While we prefer to use the alkali-metal (such as sodium or potassium) pyrophosphates and metaphosphates or the corresponding acids or acid salts, as set forth, the invention is not limited thereto, as we may use other chemicals as the alkali-metal pyro and meta-phosphites, pyro- and metarsenates. pyro- and metarsenites, or acids thereof, or other substances that possess one or both of the peculiar advantages herein noted, in particular the property of decreasing the alkalinity of the boiler water through transformations effected therein, while not interfering with, and at times aiding in maintenance of the desirable pH values in the feed water; and the property of forming relatively soluble compounds with calcium and magnesium before, but very insoluble compounds after, the transformation.

At times it may be advisable to use a mixture of pyrophosphate and metaphosphate or of alkali-metal metaphosphate and metaphosphoric acid. The presence of a small amount of pyrophosphate in the metaphosphate assures a practically neutral salt which is more readily soluble than a salt containing free metaphosphoric acid. Or it may be desired to add somewhat of orthoarsenate, metarsenate or pyroarsenate to a metaphosphate, or pyrophosphate, as when additional protection from corrosion is desired by the suitable application of electric current to the boiler water through suitable electrodes.

When phosphate and arsenate are simultaneously present in the boiler water, the calcium combines with phosphate in preference to arsenate, and thus continuity of the maintenance of the arsenate for the prevention of corrosion is assured.

The pyrophosphate or metaphosphate or other treating chemical of the character herein described, may be added to the cold feed water before it passes through the feed water heater, or it may be added to the hot water from the feed water heater before this water is pumped into the boiler, or it may be supplied in any other convenient way either to the feed water or directly to the boiler. Therefore, when we speak in the claims of supplying the boiler water with the treating chemical, we mean to include either supplying the chemical to the feed water to pass with the feed water into the boiler, or supplying the treating chemical directly to the boiler. For example, the sodium metaphosphate may be added to the cold feed water and if the feed water is not sufficiently alkaline, some alkaline reagent, such as sodium hydroxide or sodium pyrophosphate, may be added to insure sufficient alkalinity to protect the feedwater heater and feed lines against corrosion.

By taking advantage of the capability of the chemicals as above described, of being transformed in the boiler into a more acid condition, such chemicals may be injected into the boiler without destructive corrosive acid attack upon the injecting pumps and supply lines.

The rehydration of the metaphosphate and pyrophosplate present is a time action and takes place sufficiently slowly so that ordinarily the conversion into orthophosphate does not take place sufficiently to cause precipitation of calcium orthophosphate in the feed water heater. The solubility of calcium metaphosphate and calcium pyrophosphate is great enough so that there is little if any tendency for the precipitation of these calcium salts in the feed water heater.

The supplying of the metaphosphate or other chemical to the cold water has the advantage of supplying all of the treating chemicals at one point. However, when the feed water contains a relatively large amount of calcium or when the flow through the feed water heater is not rapid, it may be advantageous to add the phosphate to the feed water after it has passed beyond the feed water heater. This shortens the time during which the metaphosphate or pyrophosphate is in contact with the hot water before it enters the boiler, and allows less chance of rehydration and the formation of solid phase prior to the entry of the water into the boiler where the rehydration is desired.

The following may be cited as a specific example of the addition of the meta- or pyrophosphate and the control of the reaction so as to prevent separation of solid phase prior to the entry of the feed water into the boiler.

In a boiler plant provided with a primary feed water heater and a secondary feed water heater, such as an economizer or a heater heated by a steam bled from a turbine, the feed water is ordinarily brought to a temperature of about 212° F. in the first or primary heater, which usually has a relatively large storage capacity. The feed water is then passed through the secondary heater where its temperature may be raised to, say, 350° or 400° F., or even more, depending upon the temperature of the boiler water, and thence directly into the boiler.

Under such conditions, it is preferable to add the meta- or phyrophosphate to the feed water between the first heater and the second heater or economizer. This shortens the time during which the meta- or pyrophosphate is in contact with the water, and thus minimizes the extent of the rehydration which may begin at the temperatures encountered in the economizer or second high temperature heater. By adding the meta- or pyrophosphate at this point, the reaction does not have a chance to start in the first heater in which the retention time may be relatively long, due to the storage capacity of this heater. The water, after the addition of the meta- or pyrophosphate, is passed relatively rapidly through the economizer or second heater, so that the reaction of rehydration does not have an opportunity to go sufficiently to completion to cause objectionable separation of solid phase in the economizer or second heater.

Also, while the invention has been particularly described with reference to steam boilers supplying steam for power purposes, it may be advantageously employed in the conditioning of water for other boilers, and by the term "boilers", we intend to include various devices in which water is evaporated, such as the so-called evaporators used for producing distilled water for use as feed water or the like.

Our process may also be employed in connection with pressure vessels holding solutions, the alkalinity of which it may be desired to decrease, and at the same time protect the pumping equipment or supply lines against corrosive attack. Thus, for example, a digester may be supplied with chemical having the characteristics herein described of being transformed into a condition of greater alkali-neutralizing power, whereby the supply pumps are not subjected to the acid attack and the latent acidity of the chemical is developed in the digester where desired.

While we have specifically described the preferred embodiment of our invention, it is to be understood that the invention is not limited to the hereinbefore described details, but may be otherwise embodied and practiced within the scope of the following claims.

We claim:

1. The process of treating the water in a steam boiler, which comprises supplying to the boiler water a chemical containing a molecularly dehydrated phosphate radical which is rehydrated in the water in the boiler to a condition of greater alkali-neutralizing capacity.

2. The process of treating feed water for a steam boiler provided with a feed line, which comprises supplying to the feed water a molecularly dehydrated phosphate which is rehydrated in the water in the boiler to a condition of greater alkali-neutralizing capacity, whereby the excess alkalinity in the boiler water is neutralized without proportionately decreasing the alkalinity of the water in the feed line.

3. The process of treating water for steam boilers, which comprises supplying thereto a molecularly dehydrated phosphate radical which is rehydrated in the water in the boiler to yield acid hydrogen which neutralizes excess alkalinity in the boiler, and orthophosphate which prevents the deposition of adherent boiler scale.

4. The process of treating water for steam boilers, which comprises supplying thereto a sufficient amount of a molecularly dehydrated phosphate radical to yield upon rehydration in the water in the boiler sufficient acid hydrogen to maintain an alkalinity therein between pH values of about 10 to 11½ and to yield sufficient orthophosphate to prevent the deposition of adherent boiler scale.

5. The process of treating water for steam boilers, which comprises supplying thereto a mixture containing a molecularly dehydrated phosphate and an arsenate.

6. The process of treating water for steam boilers containing a scale-forming metal of the second group of the periodic system, which comprises the steps of subjecting the feed water to a primary lime-soda ash or zeolite treatment, and subjecting the water in the boiler to a secondary treatment with a molecularly dehydrated phosphate.

7. The process of treating feed water for a boiler, which comprises supplying condensate to the boiler together with make-up water, adding a molecularly dehydrated phosphate to the mixture and passing it to the boiler.

8. The process of treating calcium- and sulphate-containing feed water for a steam boiler, which comprises maintaining the feed water at a pH value of not less than about 8 to prevent corrosion of the feed lines, and introducing into the water a molecularly dehydrated phosphate in an amount sufficient to maintain the water in the boiler at a pH value of not over about 11½ and to provide a sufficient concentration of phosphate in the water to insure the precipitation of the calcium in the boiler water as tricalcic phosphate instead of calcium sulphate.

9. The process of treating feed water for a steam boiler, which comprises supplying to the feed water a molecularly dehydrated phosphate together with an inhibitor.

10. The process of treating feed water for a steam boiler, which comprises supplying to the feed water a molecularly dehydrated phosphate together with a tannin body as an inhibitor.

11. The process of treating water for steam boilers, which comprises supplying to the water a molecularly dehydrated phosphate and a regulated amount of an alkaline reagent.

12. The process of treating water for steam boilers, which comprises supplying to the water sodium metaphosphate and a regulated amount of sodium hydroxide.

13. The process of treating water for steam boilers, which comprises supplying to the water a mixture containing a metaphosphate, a pyrophosphate, and a regulated amount of an alkaline reagent.

14. The process of treating water for steam boilers, which comprises supplying to the water a mixture containing a metaphosphate and a pyrophosphate.

15. The process of treating the water in a steam boiler, which comprises supplying to the boiler water a chemical containing an alkali metal metaphosphate.

16. The process of treating the water in a steam boiler, which comprises supplying to the boiler water a chemical containing an alkali metal pyrophosphate.

17. The process of controlling the alkalinity of a heated water solution in a pressure vessel, which comprises supplying thereto a molecularly dehydrated treating chemical which is transformed therein with a time reaction to a condition of greater alkali-neutralizing capacity, said chemical being supplied in an amount sufficient to effectively regulate their alkalinity, whereby the alkalinity in the vessel is decreased and acid attack on the supply equipment is minimized.

18. The process of controlling the alkalinity of the water in a steam boiler provided with a feed line, which comprises supplying to the feed water a molecularly dehydrated acid radical which is transformed by rehydration in heated solution with a time reaction to a form having a greater alkali-neutralizing capacity, said molecularly dehydrated radical being supplied in an amount sufficient to effectively regulate the alkalinity of the water in the boiler, whereby the alkalinity of the water in the boiler is decreased without proportionately decreasing the alkalinity of the water in the feed line, and supplying the thus-treated feed water through the feed line into the boiler.

In testimony whereof we have hereunto set our hands.

RALPH E. HALL.
HENRY A. JACKSON.

CERTIFICATE OF CORRECTION.

Patent No. 1,903,041. March 28, 1933.

RALPH E. HALL, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, line 97, beginning with the words "The addition" strike out all to and including the syllable "phate" in line 111; page 6, line 120, in the equation, for "30" first occurrence, read "3"; page 8, line 118, for "action" read "reaction"; page 9, line 101, after "line" insert the words "and supplying the thus treated feed water through the feed line into the boiler"; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of May, A. D. 1933.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.

Patented Apr. 24, 1934 1,956,515

UNITED STATES PATENT OFFICE

1,956,515

WATER SOFTENING AND WASHING

Ralph E. Hall, Mount Lebanon, Pa., assignor to Hall Laboratories, Inc., Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application March 20, 1933, Serial No. 661,787. Renewed February 26, 1934

29 Claims. (Cl. 210—23)

The present invention relates to water softening and washing, and more particularly to the softening of water by the use of an alkali-metal metaphosphate, and to washing with water which has been treated with an alkali-metal metaphosphate. This application is a continuation in part of my copending application Serial No. 629,873, filed August 22, 1932.

The natural waters, practically all of which contain some calcium and/or magnesium, can be divided roughly into two general classes, the so-called "soft" waters and the so-called "hard" waters. There is no sharp line of division between the two, and some waters lie about midway between what would be considered to be a soft water or a hard water. In general, the soft waters contain such small amounts of calcium and magnesium that they lather fairly freely upon the addition of small amounts of the ordinary fatty-acid soaps. The hard waters, on the other hand, due primarily to their higher calcium and/or magnesium contents, do not lather freely upon the addition of a small amount of soap. The calcium and magnesium exist in such waters in the form of soluble salts, usually sulphates, bicarbonates or chlorides. These salts are ionized so that the waters contain a relatively large concentration of free calcium and/or magnesium ions. When a soap is added to such hard waters the calcium or magnesium ions combine with the fatty-acid radicals of the soap to form insoluble calcium or magnesium soaps, until the free calcium and magnesium ions are reduced in concentration to their equilibrium with these soaps. Then a lather will be formed by the addition of further soap.

While the "softening" of waters is most commonly effected to render the waters better suited for washing purposes, water softening is not limited to such uses, as hard waters are softened for various other domestic and industrial purposes. Chemically speaking, the softening of a hard water consists in reducing the concentration therein of free calcium and/or magnesium ions. The degree of softening is dependent upon the extent of the diminution of the free calcium and/or magnesium ions.

There are three usual ways now in vogue for softening water. The first method is by distillation, and condensation of the steam, whereby pure water is evaporated from the impure hard water, the impurities remaining behind. This requires distillation apparatus and is relatively expensive. The second method is by the use of the so-called water-softening compounds, generally sodium carbonate (washing soda), trisodium phosphate which is sold under various trade names, lime-soda ash, sodium silicate, etc. In these processes the calcium and magnesium are converted, for the most part, into insoluble salts which are precipitated and which may be removed, although in the ordinary domestic use of water softeners the precipitate remains in the softened water. Practically all of these water-softening compounds are highly alkaline, and water softened by their use is rendered highly alkaline which is objectionable for many purposes, such, for example, as for domestic use, as the alkalinity attacks the human skin and the fibres of fabrics being washed. When the precipitated solid phase remains in the softened water, as is usual in domestic use of water-softening compounds, the soap will tend to redissolve the precipitated phase, such as the calcium carbonate or calcium phosphate, and re-precipitate the calcium as calcium soap, unless a large excess of sodium carbonate or sodium phosphate is used. It is therefore necessary, for such domestic water softening, to use a large excess of the water-softening compound with a consequent excessive alkalinity imparted to the softened water. Also, the solid phase remains in the water and may be entrapped in the fabrics being washed, rendering them harsh. The third common method of softening water now in vogue is the zeolite or base exchange method, in which the water is passed through a special softening apparatus in which the sodium of the zeolite is exchanged for the calcium and/or magnesium in the water. The zeolite process requires the use of relatively expensive apparatus which requires attention in order to periodically regenerate the zeolite.

I have found that waters containing calcium and/or magnesium may be effectively softened by the use of an alkali-metal metaphosphate, such as sodium metaphosphate, potassium metaphosphate, lithium metaphosphate, or ammonium metaphosphate, preferably sodium metaphosphate on account of its lesser cost. For purposes of conciseness in description, my process will be described with reference to the use of sodium metaphosphate, it being understood that other alkali-metal metaphosphates may be used.

I have found that the softening thus effected can be had without objectionably increasing, or increasing at all, the alkalinity of the water. In fact, a neutral softened water can be obtained, or a softened water which is slightly acid or which is alkaline to the desired extent. Also, softening can be effected without the production of any solid-phase precipitate which would cloud the water, and a completely softened water can be obtained which is crystal clear. The process can be carried out without the use of any special equipment, the sodium metaphosphate or a solution thereof simply being added to the water. This adapts it particularly to domestic use. The domestic user can obtain a completely softened water which is crystal clear and in which the alkalinity is not increased, so that it can be used without damage to the skin or to fabrics.

When the water is to be used for washing purposes, a soap will ordinarily be added to increase its detergent and deflocculative properties and assist in peptizing greases. However, the softened water may be used for any purpose for which soft water is desired. For certain purposes the water which has been softened with an alkali-metal metaphosphate is superior to a naturally soft wa~~ter or a wate~~r which has been softened by the usual water-softening methods, in that the alkali-metal metaphosphate imparts to the water certain detergent properties and also solvent properties, particularly upon calcium and magnesium soaps. Water containing the alkali-metal metaphosphate may be advantageously used for rinse water in the laundering of fabrics since, due to the solvent properties of the metaphosphate for such soaps, it dissolves calcium and magnesium soaps which may have been deposited in the fabrics in the previous washing operation.

The material which I prefer to use is the soluble sodium metaphosphate sometimes called "Graham's salt", which may have mixed with it a small amount of sodium phyrophosphate to counteract the slight acidity of the sodium metaphosphate. Graham's salt is believed to consist principally of sodium hexametaphosphate. The sodium hexametaphosphate is assumed to be a complex of the general formula $Na_2(Na_4P_6O_{18})$, although some authorities believe that salts of the formula $Na_5(NaP_6O_{18})$ and $Na_4(Na_2P_6O_{18})$ may also be present.

Sodium hexametaphosphate in readily soluble form may be prepared by strongly heating monosodium dihydrogen orthophosphate, and rapidly cooling the molten mass. The quick cooling is apparently essential to the formation of a readily soluble salt. Upon slower cooling of the molten mass there is a tendency to form other sodium metaphosphates, such as sodium trimetaphosphate which is soluble, and sodium monometaphosphate which is difficultly soluble. I prefer to cool the mass sufficiently rapidly so that the sodium metaphosphate is obtained principally in the form generally accepted as sodium hexametaphosphate. While I prefer to use sodium hexametaphosphate, other metaphosphates may be employed, such as the trimetaphosphates.

The sodium hexametaphosphate is slightly acid, and I therefore prefer to form it so that it will contain a small amount of sodium pyrophosphate, which is slightly alkaline, in order to obtain a water softener which is substantially neutral. The addition of a small amount of sodium carbonate to the monosodium dihydrogen orthophosphate at the time of fusion, results in the presence of an equivalent amount of sodium pyrophosphate in the fused product, and the amount of sodium carbonate used will determine the neutrality or slight alkalinity of the fused product. Provision for neutralizing the acidity of the sodium metaphosphate when it is dissolved may also be made, if desired, by mixing with it a small amount of caustic soda, sodium carbonate, or sesquicarbonate, borax, trisodium phosphate, sodium metasilicate, etc. The amounts of such neutralizing agents are relatively small and my water softener consists principally of sodium metaphosphate, and therefore when I speak of sodium metaphosphate I mean to include not only the pure sodium metaphosphate, but also sodium metaphosphate containing small amounts of acid-neutralizing reagents and perhaps other impurities.

The action of the sodium metaphosphate is different from that of the usual water-softening compounds. No permanent precipitate of calcium or magnesium is formed. I believe that the sodium metaphosphate softens the water through removing the free calcium and magnesium ions by bringing them into a soluble slightly ionized compound or radical. The following experimental evidence points to this explanation of the action of the sodium metaphosphate.

If the proper amount of sodium metaphosphate is added to a hard calcium-bicarbonate water, and the water is then boiled to drive off the carbon dioxide, no precipitate of calcium carbonate is formed. This indicates that the calcium is combined in some slightly ionized compound or radical, whereby the calcium-ion concentration is reduced below below that corresponding to the saturation equilibrium of calcium carbonate. It is possible to add sodium metaphosphate to a mixture of water and solid calcium carbonate and to dissolve the calcium carbonate, forming a clear solution. Sodium metaphosphate may be added to a mixture of water and tricalcic phosphate and the same phenomenon will occur, demonstrating the extremely low ionization of the soluble compound or radical in which the calcium is sequestered or locked up, so to speak.

Further evidence of the almost complete removal of the free calcium and magnesium ions by sodium metaphosphate is furnished by the addition of sodium metaphosphate to a hard water to which soap has been added, forming the well-known scum of calcium and/or magnesium soap. If a sodium metaphosphate is added to such water in appropriate amount it will cause complete dissolution of the calcium and/or magnesium soap, freeing the fatty-acid ions from the calcium and/or magnesium and thus rendering them available for detergent action. This demonstrates that the ionization of the soluble compound formed by the sodium metaphosphate with the calcium and/or magnesium is such that the calcium-ion and/or magnesium ion concentration resulting therefrom is less than that from the saturated solution of calcium and/or magnesium oleate or other calcium and/or magnesium salt of the fatty acids commonly used in soaps.

In softening water for washing purposes, the sodium metaphosphate is added in an amount sufficient to effect a satisfactory degree of softening of the water against soap. The simplest way of determining the amount of sodium metaphosphate required for any particular water is to simply keep on adding the sodium metaphosphate until the water is softened to the degree effective for the purpose in hand. The usual way of determining softness is by the familiar soap test. If the water gives a permanent lather upon the addition of a small amount of soap, it is considered to be completely softened. However, for many purposes complete softening of the water is not required, as washing may be carried out with an incompletely softened water. In fact, in the domestic use of water-softening compounds, the housewife often does not add enough of the compound to effect complete softening, but does add enough so that a lather is produced upon the addition of soap, although the lather may not be permanent. Therefore, while it is preferred to add sufficient sodium metaphosphate to effect complete softening, smaller amounts of sodium metaphosphate may be used which will not completely soften the water but which will soften the water enough to satisfy the user. Therefore, when I speak of effectively suppressing the calcium-ion concentration, I do not mean that complete softening of the water must be attained, as partial softening may be sufficient to suppress the calcium-ion concentration effectively enough for the purpose desired by the user.

The domestic user will use the sodium metaphosphate exactly as he or she uses washing soda or trisodium phosphate, namely, adding the amount which experience has shown will give proper lathering qualities to the water. The commercial user, such as laundries or textile establishments, will add measured amounts of the sodium metaphosphate to measured amounts of water until the standard soap test indicates complete softening of the water. This will tell the user the minimum amount of sodium metaphosphate required to soften his particular hard water.

As a specific example to indicate generally the amount of the sodium metaphosphate required for softening a typical hard water for washing purposes, I may cite the case of the Pittsburgh city water which, when tested, contained approximately 30 parts per million of calcium and approximately 4 parts per million of magnesium. This water was completely softened by the addition per 1000 gallons of 3 pounds of sodium hexametaphosphate containing about 10% sodium pyrophosphate to render it substantially neutral.

One of the most important applications of my process of water-softening is that of softening the water against soap, on account of the extensive use of hard waters for domestic and industrial purposes. The addition of the sodium metaphosphate not only completely softens the water against soap so as to completely prevent the formation of insoluble calcium and magnesium soaps, but effects this softening without the formation of any solid precipitates of calcium and magnesium and without rendering the water alkaline, as is the case with sodium carbonate, trisodium phosphate, and sodium silicate, which are commonly used as water softening compounds. The advantages of obtaining a perfectly softened crystal clear neutral water are too obvious to require extended discussion. It may be mentioned, however, that, as shown by the ability of the solution of sodium metaphosphate to actually dissolve calcium carbonate, tricalcic phosphate and calcium silicate, the water is actually softened to a greater degree than that obtainable by the use of sodium carbonate, trisodium phosphate or sodium silicate. The water which has been softened in accordance with my process can be used advantageously for any washing purposes, such as for washing fabrics, hair, the body, dishes, walls, painted or varnished surfaces, etc., particularly since complete softening is effected without any undesirable increase in alkalinity.

Another important application is in the rinsing of clothes in laundering. The water softened in accordance with my process not only rinses out the soapy water carried over from the washing tub, but also dissolves calcium and/or magnesium soaps which may be carried with the clothes. If the washing of the clothes is carried out with hard water or with an incompletely softened water, a curd-like calcium and/or magnesium soap is formed which may be carried over into the rinse with the clothes. As stated above, the solution of sodium metaphosphate will dissolve such calcium and/or magnesium soap and remove it from the clothes. Therefore, as a rinse water, particularly where calcium and/or magnesium soap may be carried over with the clothes from the washing water, the water softened in accordance with my process is even more effective as a rinse than a naturally soft water.

My process of water softening, however, has other applications. For example, the trouble encountered in the canning industry in using water to cool and wash cans taken from the pressure cookers may be overcome. At the present time the cans which are taken from the pressure cookers are immersed in water to cool them. If the water is one containing considerable calcium bicarbonate, the heating of the water by the hot cans results in driving off the carbon dioxide, causing a precipitation of calcium carbonate which will be deposited and dull or "gray" the cans. This trouble may be completely overcome by adding sufficient sodium metaphosphate to the water to prevent the formation of calcium carbonate when the water is heated.

Another application of my process of water softening is in the artificial ice industry. As the ice is frozen, crystals of pure water are formed and the carbon dioxide of the water is driven off as a gas. This results in breaking down calcium bicarbonate if present in the water, resulting in cloudiness in the ice. This may be overcome by the addition of sufficient sodium metaphosphate to prevent the formation of calcium carbonate in the ice.

Another application of my waste-softening process is in the prevention and even dissolution of sludge or scale deposits in the feed-line equipment for steam boilers. As described in the United States patent of Hall and Jackson, No. 1,903,041, dated March 28, 1933, the alkalinity of water in the steam boiler may be controlled by the addition of sodium metaphosphate to the boiler water, usually by addition to the feed water as it passes through the boiler feed lines. As described by Hall and Jackson, the sodium metaphosphate is converted in the boiler into sodium orthophosphate which combines with the calcium to form a sludge of tricalcic orthophosphate in the boiler. When the sodium metaphosphate or sodium pyrophosphate, or a mixture of the two, is added to the feed water as described by Hall and Jackson, not enough of the phosphate is added to soften the water, as the amount of orthophosphate required to precipitate the calcium as calcium orthophosphate in the boiler contains a smaller amount of P_2O_5 than the amount of P_2O_5 required in the form of metaphosphate to soften the water. As a consequence, in feeding the water to the boiler as described by Hall and Jackson, because some transformation of metaphosphate or pyrophosphate to orthophosphate occurs in the feed lines, difficulties may be encountered due to the deposition of tricalcic-phosphate scale or sludge in the feed line equipment. The remedy suggested by Hall and Jackson of adding an inhibitor, such as a tannin body, is objectionable as introducing unnecessary organic matter into the boiler water.

I have found that the trouble encountered with feed line deposits may be completely overcome in most cases, by adding enough sodium metaphosphate to the feed water to completely soften the water passing through the feed line equipment. Such amount, if continuously added would be far in excess of that required for the boiler, and for that reason I add the sodium metaphosphate to the feed water intermittently. As a specific example, the sodium metaphosphate may be added to the feed water for, say, a 5 or 10 minute period during each hour of a continuous feed of feed water. This permits sufficient sodium metaphosphate to be added to the feed water during such 5 or 10 minutes to completely soften the water as against tricalcic phosphate and prevents the deposition of any tricalcic phosphate in the feed lines. Moreover, since the calcium-ion concentration of the feed water to which this excess amount of sodium metaphosphate has been added is less than that in equilibrium with solid tricalcic phosphate or calcium carbonate, the water containing the excess sodium metaphosphate will actually dissolve any phosphate or carbonate which may be deposited in the feed lines. Calcium carbonate may be deposited in the feed lines during the time when untreated water is being pumped to the boiler, but any such deposits are eliminated by their dissolution when the water which is completely softened by the sodium metaphosphate is passed through the feed line. This application of my process of water softening illustrates the completeness to which the water softening can be carried by the use of a proper amount of sodium metaphosphate, since the concentration of calcium and magnesium ions is reduced to the point where the water will actually redissolve tricalcic phosphate and calcium carbonate. The water treated with the sodium metaphosphate is even more efficacious in dissolving such lime deposits than would be distilled water, since the sodium metaphosphate removes from the solution the calcium and magnesium ions coming from the feed-line deposits and thus keeps the water in an undersaturated condition with respect to the calcium phosphate or calcium carbonate deposits.

Another application of my process of water softening is in the prevention and dissolution of sludge or scale deposits in hot water distributing systems. The calcium derived from the water or by the dissolution of any solid deposits in the pipes is apparently locked up in the extremely slightly ionized compound or radical which it forms with the metaphosphate. Thus a soft and clear water is delivered at the point of use, and the deposition of scale is prevented and previously deposited scale is redissolved.

The foregoing specific description relates particularly to the suppression of calcium-ions in the hard water. The calcium is the principal precipitate-forming alkaline-earth metal in most hard waters, although it is frequently accompanied with magnesium. I therefore use the expression "alkaline-earth metals" as inclusive of magnesium as well as calcium. The sodium metaphosphate forms soluble slightly ionized compounds with magnesium, reducing its free-ion concentration in the same way as it reduces the free-ion concentration of calcium. Any hardness due to magnesium is overcome in the same way as the calcium hardness, by addition of the requisite amount of sodium metaphosphate. Ordinarily, sodium metaphosphate is added until the particular water in question is shown to be soft by the soap test, indicating that the proper amount of sodium metaphosphate has been added to take care of all of the insoluble soap-forming metal ions.

I have found that the sodium pyrophosphate although exerting some influence in suppressing the calcium-ion concentration, is nevertheless relatively ineffective in softening calcium-containing waters compared with sodium metaphosphate. In order to get efficient softening of calcium-containing waters, I have found that sodium metaphosphate is required, as excessive amounts of sodium pyrophosphate would be necessary to get an equal degree of softening. Sodium pyrophosphate, however, has considerable softening effect so far as magnesium is concerned. Sodium pyrophosphate is somewhat alkaline. I prefer to use a relatively small amount, say, about 10% of sodium pyrophosphate in the sodium metaphosphate. The pyrophosphate not only neutralizes the acidity of the metaphosphate, but has some action in softening the water, particularly on the magnesium.

The amount of pyrophosphate or other acid-neutralizing reagent, such, for example, as sodium hydrate or sodium carbonate, may be regulated in accordance with the desired neutrality or alkalinity of the softened water. For the majority of purposes only enough acid-neutralizing reagent is added to the sodium metaphosphate to insure neutrality or very slight alkalinity, since for most purposes a neutral or very slightly alkaline softened water is desired.

I have found that as the alkalinity of the water is increased, the amount of sodium metaphosphate required for softening is increased. For example, a given water which required 1.7 pounds of sodium hexametaphosphate per 1000 gallons for softening against soap at a pH value of 8.5 required 2.9 pounds at a pH value of 10 for a like degree of softness. I therefore prefer to prevent excessive alkalinity not only because a neutral or but slightly alkaline water is best for most purposes, such as washing, but also because a neutral or but slightly alkaline water is more effectively and economically softened by my process than is a highly alkaline water.

While I prefer to use sodium metaphosphate, other alkali-metal metaphosphates may be used, such, for example, as potassium metaphosphate, lithium metaphosphate and ammonium metaphosphate. All of these metaphosphates are preferably used in the soluble form commonly known as hexametaphosphate.

The material may be sold as the metaphosphate mixed with a small amount of pyrophosphate or some alkaline substance, such as borax, sodium carbonate or trisodium phosphate, to neutralize the slight acidity of metaphosphate. However, the material may be sold in other combinations, such as washing compound containing sodium metaphosphate and a soap. The relatively low alkalinity of such compounds permits the use of perfumes, which could not be used in the more highly alkaline washing preparations.

If desired, the sodium metaphosphate may be mixed with a substance which, when dissolved therewith, will act as a buffering agent to stabilize the water against too great acidity or too great alkalinity. For example, the sodium metaphosphate may be mixed with sodium bicarbonate, or mixed with sodium bicarbonate plus a small amount of sodium carbonate as in the sodium sesqui-carbonate, or mixed with disodium phosphate. These salts will have the well-known buffering action to stabilize the water against too great acidity or alkalinity.

While I do not know with certainty the exact chemical reactions occurring, I believe that the chemical reactions probably occur as I will now describe them. The following explanation is in accordance with the observed facts and is given as a theoretical discussion of what I believe occurs. It will be understood, therefore, that the invention is not limited to this theoretical explanation.

If a solution of sodium hexametaphosphate is slowly added to a hard water containing sufficient calcium, a white cloudy precipitate is first formed. I believe that this precipitate is calcium metaphosphate whose simplest formula might be expressed as $Ca(PO_3)_2$. To obtain calcium methaphosphate 2 formula weights of sodium metaphosphate ($NaPO_3$) are required to 1 formula weight of calcium (Ca). The experimental work on sodium hexametaphosphate indicates that it probably has the molecular formula $(Na_2(Na_4P_6O_{18})$. I believe that the calcium metaphosphate probably has a similarly constituted molecule expressed by the formula $Ca(Ca_2P_6O_{18})$. The calcium which is outside of the parenthesis in this formula probably ionizes in a degree similar to that characteristic of the salts composed of divalent metal and divalent radical.

At this point not only is there an objectionable precipitate, but complete softening has not been attained. In order to get effective softening, the sodium hexametaphosphate is required in excess of that to theoretically combine with the calcium to form calcium metaphosphate $Ca(PO_3)_2$. Upon the addition of sodium hexametaphosphate in excess of the theoretical combining formula weights, the precipitate is redissolved, and the water is softened as indicated by the soap test. For the re-solution of the precipitate, I believe that at least 1 additional formula weight of sodium metaphosphate should be used above that required to theoretically combine with the calcium as calcium metaphosphate. As this additional sodium metaphosphate is added, I believe that a combination is formed corresponding to the salt $Na_2(Ca_2P_6O_{18})$. This salt is probably ionized, yielding the sodium radical and a $Ca_2P_6O_{18}$ radical. The latter radical, in turn, is also probably ionized to a slight extent, yielding free calcium ions. The extent to which ionization of this radical occurs appears to be governed by the excess of sodium metaphosphate employed. The addition of sodium metaphosphate to supply 3 formula weights of sodium metaphosphate ($NaPO_3$) to 1 formula weight of calcium (Ca), softens the water to considerable extent, and apparently softens it against calcium carbonate, but not against soap. The addition of another formula weight of sodium metaphosphate to give 4 formula weights of sodium metaphosphate to 1 formula weight of calcium, was sufficient to soften a water containing 20 parts per million of calcium at a pH value of 8.5, but 7 formula weights of the sodium metaphosphate were required for this amount of calcium when the pH value was 10. My present experimental work indicates that 4 formula weights of sodium metaphosphate ($NaPO_3$) to 1 formula weight of calcium (Ca) is approximately the minimum which can be used for effective softening of water against soap.

The water softening action of the sodium metaphosphate is not that of throwing the calcium out of solution as an insoluble precipitate as is the case of the usual water softening compounds, but is rather to sequester or lock up the calcium in a but extremely slightly ionizable condition in a soluble sodium-calcium-metaphosphate complex molecule.

Magnesium probably forms a corresponding complex radical with the sodium hexametaphosphate, which, like the calcium-containing radical, has but a slight degree of ionization, which may be repressed by an excess of the sodium hexametaphosphate corresponding to the excess required to repress the ionization of the calcium.

The water softened in accordance with my process may be considered as a new product, in that it may be completely softened while at the same time containing in solution an amount of calcium which, if not held in a substantially un-ionized radical, would render the water hard. Ordinarily, if water contains in solution over about 5 parts per million of calcium, it is not considered to be completely soft as against a fatty acid soap, since it will consume some of the soap before a permanent lather is produced. By my process I can produce a water which will contain more than 5 parts per million of calcium in solution and which, at the same time, is completely softened as against a fatty acid soap.

The water which has been softened by the addition of the alkali-metal metaphosphate in accordance with my process, has certain further advantages, particularly for detergent and certain solvent purposes. It has greater detergent properties than a naturally soft water. The metaphosphate apparently imparts to the water a detergent or deflocculating action upon soil, which is the usual technical expression for dirt, grease and other substances to be removed. It increases the detergent action of even a soft water, so that it may be advantageously added to soft water for washing purposes.

The water to which the metaphosphate has been added can be advantageously used in places where it may not be desirable to employ a soapy water, such, for example, as in the washing of bottles, silverware, windows, automobiles, greasy metal parts, etc.

It can be advantageously employed for the "break" in laundering. In the usual commercial laundries the soiled clothes are put into the laundering wheel and are first subjected to a preliminary agitation or washing in cold or lukewarm water, usually made slightly alkaline with a small amount of an alkaline reagent, such as sodium carbonate or sodium metasilicate, and sometimes with the addition of a small amount of soap. This treatment is called the "break", and is employed to dislodge and remove the more readily removable soil prior to the softening of the fibers with the soap and hot water in the washing operation which immediately follows the break. In most commercial laundries either a naturally soft water or an artificially softened water, such as a zeolite softened water, is used for the break. It has been found that such a softened water picks up enough calcium from the clothes so that it frequently becomes quite hard at the end of the break when the water is drained off. The water which has been treated with an alkali-metal metaphosphate can be used in the break with a considerable advantage over the ordinary soft or softened waters. The metaphosphate treated water not only has inherent detergent properties, but also has solvent properties on the calcium. It not only tends more completely to dissolve out calcium compounds from the clothes and the soil than an ordinary softened water, but, because the dissolved calcium is locked up or sequestered in a but slightly ionized condition, the water will remain soft throughout the entire break.

At the end of the break the water is never completely removed from the clothes and the wet clothes remain in the wheel for the subsequent washing operation. The metaphosphate-treated water which remains in the clothes after the break is carried along into the next or soap-washing step and assists in effecting softening of the water for this step.

The calcium in the soiled clothes frequently exists in considerable part as calcium soap from previous launderings. By using the alkali-metal metaphosphate in the break, such calcium soap is dissolved in the break, and the clothes go to the washing operation freed from such calcium soap. Also, the metaphosphate exerts a solvent action on the soil which exists principally in the form of fine particles of dirt in the clothes.

The water to which the metaphosphate has been added can be advantageously used in de-liming processes because of the lime-solvent action of the metaphosphate. It is particularly useful where the properties of de-liming are required combined with a detergent action, as in the washing of hides and leather which have been treated with lime and from which it is desired to also remove dirt and grease. It not only increases the detergent action of a soft water, but renders it much more effective in dissolving substances like lime and calcareous compounds.

In the foregoing discussion I have spoken of the softening of water against soaps, with particular reference to the ordinary soaps which are usually of the fatty-acid type and which will combine with lime to form a curd-like calcium soap. There are certain recently developed soaps of the sulphated alcohol type, known under various trade names such as "Gardinol", "Igepon", "Brilliant Avirol" and "Orvus", which will lather in hard water. They do not soften a hard water, and the water remains essentially hard during the washing operation and has a harsh "feel" even though a lather may be formed. I have found that water softened by my process may be used with advantage with the sulphated alcohol types of soap, as the water has an increased detergent effect and also probably renders the sulphated alcohol type of soap more effective by preventing its combination with the calcium. When a soap of this type is used, the water may not always be softened to the same degree as for use with the fatty-acid soaps.

While I have described a number of applications and the preferred embodiment of my invention, and have set forth what I believe to be the correct theoretical explanation of the chemistry involved, it is to be understood that the invention is not limited to such applications, or to its preferred embodiment or to my theoretical explanation, but that the invention may be otherwise embodied and practiced within the scope of the following claims.

I claim:

1. The process of softening water containing an alkaline-earth metal compound, which comprises adding thereto an alkali-metal metaphosphate in an amount sufficient to effectively suppress the soap-consuming alkaline-earth metal ion concentration.

2. The process of softening calcium-containing waters, which comprises adding thereto sodium metaphosphate in an amount sufficient to effectively suppress the calcium-ion concentration.

3. The process of softening calcium-containing waters, which comprises adding thereto at least about 4 formula weights of sodium metaphosphate ($NaPO_3$) to 1 formula weight of calcuim (Ca).

4. The process of softening calcium-containing waters, which comprises adding thereto an alkali-metal metaphosphate in an amount sufficient to reduce the calcium-ion concentration below that in equilibrium with the solid phase of its fatty acid soap.

5. The process of softening calcium-containing waters, which consists in adding thereto an alkali-metal metaphosphate in an amount sufficient to reduce the calcium-ion concentration below that in equilibrium with the solid phase of calcium carbonate.

6. The process of softening calcium-containing waters, which consists in adding thereto an alkali-metal metaphosphate in an amount sufficient to reduce the calcium-ion concentration below that in equilibrium with the solid phase of tricalcic phosphate.

7. The process of preventing deposits of calcium carbonate or calcium phosphate in feed lines of steam boilers, which comprises intermittently supplying through the feed line, water containing an alkali-metal metaphosphate in an amount sufficient to repress the calcium-ion concentration below that in equilibrium with the precipitate to be prevented.

8. The process of supplying water to steam boilers through feed-line equipment, which comprises passing through the feed-line equipment to the boiler, feed water which periodically contains sufficient sodium metaphosphate to prevent deposition of feed-line deposits, and between such periods supplying feed water untreated with phosphate.

9. The process of washing, which comprises adding to a hard water a sufficient amount of alkali-metal metaphosphate to soften it, and washing the materials to be cleansed with the thus-softened water.

10. The process of washing, which comprises adding to a hard water a sufficient amount of alkali-metal metaphosphate to soften it, adding a soap to the water, and washing the materials to be cleansed with the water thus treated.

11. The process of washing, which comprises adding an alkali-metal metaphosphate to water, and washing the materials to be cleansed with the water so treated.

12. The process of dissolving deposits of alkaline-earth metal compounds, which comprises subjecting them to the solvent action of water containing an alkali-metal metaphosphate.

13. The process of dissolving deposits of calcium soap, which comprises subjecting them to the solvent action of water containing an alkali-metal metaphosphate.

14. In the process of laundering fabrics, the step which consists in rinsing the fabrics with rinse water containing an alkali-metal metaphosphate which exerts a solvent action upon alkaline-earth metal soaps which may have been deposited in the fabrics.

15. In the process of laundering clothes, the step which consists in subjecting the clothes in the break to water containing an alkali-metal metaphosphate.

16. As a washing compound, a mixture con-

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taining an alkali-metal metaphosphate and a soap.

17. As a water-softening compound, a mixture containing sodium metaphosphate and a buffering salt to prevent too great acidity or alkalinity in the softened water.

18. As a new product, a water having more than 5 parts per million of calcium in solution, but which is completely softened against a fatty acid soap.

19. The process of washing, which comprises adding an alkali-metal metaphosphate and soap to water, and washing the materials to be cleansed with the water thus treated.

20. The process of softening water containing an alkaline-earth metal compound, which comprises adding thereto an alkali-metal metaphosphate in an amount sufficient to combine with the alkaline-earth metal and form a soluble slightly ionized complex therewith while maintaining the water free from excess alkalinity, whereby a soft clear water without excess alkalinity is secured.

21. As a new product, a soft water having more than 5 parts per million of calcium held in solution by metaphosphate and characterized by freedom from calcium precipitates and freedom from excess alkalinity.

22. The process of treating water containing an alkaline-earth metal compound, which comprises adding to the water alkali-metal metaphosphate in an amount sufficient to hold the alkaline-earth metal in a soluble slightly ionized metaphosphate complex.

23. The process of washing, which consists in washing the materials to be cleansed with water and sequestering the alkaline earth metal constituents of alkaline earth metal compounds present into water-soluble slightly ionized metaphosphate complexes while subjecting the materials to the action of a detergent, whereby alkaline earth metal compounds which may be present in the materials are removed therefrom and the washing is effected without the formation of solid alkaline earth metal-containing precipitates and is thereby facilitated.

24. A water softening preparation containing an alkali-metal metaphosphate as an essential ingredient.

25. A water softening compound containing effective amounts of an alkali-metal metaphosphate and an alkali-metal pyrophosphate.

26. A water softening compound containing effective amounts of an alkali-metal metaphosphate and a reagent for neutralizing the acidity of the metaphosphate.

27. A water softener which softens calcium-containing waters without precipitation or removal of the calcium, consisting principally of sodium metaphosphate.

28. A washing composition comprising an alkali-metal metaphosphate and a deflocculative detergent capable of peptizing greases.

29. The process of washing, which comprises washing the material to be cleansed with water and sequestering the calcium of calcium compounds present into water soluble slightly ionized complexes while subjecting the material to the action of a detergent.

RALPH E. HALL.

Nº 7958 A.D. 1892

Date of Application, 27th Apr., 1892
Complete Specification Left, 2nd Jan., 1893—Accepted, 25th Feb., 1893

PROVISIONAL SPECIFICATION.

A Process for the Production of Phosphates of Potassium or Aluminium Soluble in Water.

I, Dr. Heinrich Precht of New Stassfurt, in the Empire of Germany Doctor of Philosophy, do hereby declare the nature of this invention to be as follows:—

The ordinary metaphosphate of potassium which may be obtained by known methods, such for instance as by melting together phosphoric acid and carbonate of potassium or potash or chloride of potassium, or by heating orthophosphate of potassium, one third saturated, to a red heat is almost insoluble in water.

By my invention however I obtain this salt in a combination which is easily soluble in water and which contains the whole of the phosphoric acid of the salt in a form which is easily soluble in water.

In carrying out my invention I convert insoluble metaphosphate of potassium into the soluble condition by melting the metaphosphate of potassium which is insoluble in water, and cooling the fused mass rapidly, by which means the fused material is prevented from passing into the crystalline condition, and soluble metaphosphate of potash is produced.

Or by fusing metaphosphate of potassium insoluble in water with chloride of potassium at a red heat in the presence of the vapour of water, whereby, as the result of the action of the water vapour upon the fused mixture, pyrophosphate of potassium soluble in water is produced.

I employ the soluble metaphosphate or pyrophosphate of potassium obtained as described for rendering insoluble phosphate of aluminium soluble in water by fusing the latter with metaphosphate or pyrophosphate of potassium or a mixture of the two, and I employ the soluble phosphates of potassium obtained as described for the production of orthophosphate of potassium either by heating a watery solution of these salts under pressure, or by heating pyrophosphate of potassium obtained as described (with which the soluble metaphosphate of potassium obtained as described can be mixed) in a watery solution with so much phosphoric acid that one molecule of the latter is present to each molecule of potash, whereupon the formation of monopotassic orthophospate occurs.

Dated the 27th day of April 1892.

G. F. REDFERN & Co.,
4, South Street, Finsbury, London, Agents for the Applicant.

COMPLETE SPECIFICATION.

A Process for the Production of Phosphates of Potassium or Aluminium Soluble in Water.

I, Dr. Heinrich Precht, of New Stassfurt, in the Empire of Germany, Doctor of Philosophy do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The ordinary metaphosphate of potassium which may be obtained by known methods, such for instance as by melting together phosphoric acid and carbonate of potassium or potash or chloride of potassium, or by heating orthophosphate of potassium, one third saturated to a red heat is almost insoluble in water.

[*Price 8d.*]

By my invention however I obtain this salt in a combination which is easily soluble in water and which contains the whole of the phosphoric acid of the salt in a form which is easily soluble in water.

This object may be attained by subjecting metaphosphate of potassium to a smelting process as hereinafter described. If the process be so conducted as to cool the melted metaphosphate very rapidly, there results an easily soluble amorphous potassium salt of the condensed metaphosphoric acid. If however the process be carried out by melting together metaphosphate of potassium and chloride of potassium, and allowing the vapour of water to act upon the melted materials, a phosphate of potassium which is soluble in water is obtained chiefly pyrophosphate of potassium.

My process is carried out as follows:—

The insoluble metaphosphate of potassium is fused at a red heat, and is caused to set rapidly by allowing it to run out into shallow iron boxes or moulds, so that it remains in an amorphous condition, and does not become crystalline. By this process is formed the potassium salt of the condensed metaphosphoric acid, and this if allowed to cool slowly would pass into a crystalline and insoluble condition. The fusing of the insoluble metaphosphate of potassium is most conveniently carried out in a reverberatory furnace, in which the metaphosphate of potassium is heated to such a point that it can be drawn off in a liquid condition through a vent hole. If the insoluble metaphosphate be melted in a furnace with an inclined hearth, the process may be carried on continuously by inserting the phosphate which is to be treated at the coolest part of the furnace, on the hearth inclined toward the flame, passing it forward by means of rakes, so that the salt gradually attains the fluid condition by the heat of the furnace, and the fused phosphate is allowed to flow continuously out at the hottest part of the furnace. It is advisable to allow an oxidizing flame to act upon the phosphate for the purpose of fusing it, since the reducing flame might give rise to a reduction of the phosphoric acid and thus cause loss. Experiments have shewn that a phosphate of potassium which is perfectly soluble in water is formed if one molecule of phosphoric acid and one molecule of potash or if at least 66·2 parts by weight of the latter to 100 of anhydrous phosphoric acid are present in the fused mass. In practice it is advantageous to work with a larger proportion of potash, so that the phosphoric acid in the fused mass is present partly in the condition of pyrophosphate of potassium. If the proportions of potash and phosphoric acid were such that 1 part of pyrophosphate of potassium must of necessity be formed to 4 parts of metaphosphate of potassium, the process above described results in the production of perfectly soluble phosphate of potassium. If it be desired to obtain such a proportion in the fused mass the required quantity of a basic substance such as potash or soda may be added during the process of melting. If for the manufacture of soluble phosphate of potassium from insoluble metaphosphate of potassium the latter is to be fused with chloride of potassium, the presence of the vapour of water during the process is indispensable, since the product then consists chiefly of soluble pyrophosphate of potassium. In the above case, 1 molecule or 236 parts by weight, of metaphosphate of potassium is melted with 2 molecules or 149 parts by weight of chloride of potassium and the vapour of water is allowed to act upon the fused mass; by the aid of the water soluble pyrophosphate of potassium is formed, as shewn by the following equation:—$K_2OP_2O_5 + 2\,KCl + H_2O = 2\,(K_2O)\,P_2O_5 + 2\,HCl$. The vapour of water required for this reaction may be passed either into or over the fused mass; in the latter case, it may be brought into contact with the fused mass in the gases of combustion which play over the mixture of salts by employing moist fuel.

The soluble phosphate of potassium obtained by the foregoing process may now be employed in accordance with my invention for the manufacture of a phosphate of aluminium which is soluble in water, and also of orthophosphate of potassium by the means now to be described. For the manufacture of aluminium phosphate

soluble in water the phosphate of aluminium to be acted upon is mixed with the phosphate of potassium soluble in water obtained in the preceding process (that is to say, with pyro- or meta-phosphate of potassium soluble in water) in any proportion desired, provided always that the mixture does not contain more than 40 °/o of phosphate of aluminium. The meta- or pyrophosphate of potash, soluble in water, obtained by the process previously described, forms with phosphate of aluminium compounds which are soluble in water, and of which a watery solution does not decompose. The phosphate of aluminium to be employed in this process is either added as such in its usual insoluble state during the fusion, or added to the phosphates of potassium in the phosphoric acid solution which serves as the liberating agent, by employing for the preparation of insoluble phosphate of potassium a phosphoric acid which contains phosphate of aluminium as an impurity. If the phosphate of aluminium contains phosphate of iron in small quantity as an impurity, the latter also assumes the soluble form. In employing meta- or pyrophosphate of potassium soluble in water, prepared according to my invention, for the manufacture of orthophosphate of potassium these salts are dissolved in water to make a solution of a degree of concentration corresponding with a specific gravity of about 1·25 and heated under pressure, by means of high pressure steam in a closed vessel, it may be, to a temperature beyond their boiling point. The higher the temperature, the more rapidly does the conversion proceed, at 120° C. it is complete in about two hours. The reaction may be accelerated by the addition of phosphoric acid. By adding phosphoric acid when pyrophosphate of potassium is being employed prepared as hereinbefore described which pyrophosphate may also be mixed with metaphosphate of potassium made soluble according to the foregoing invention, the employment of pressure may be dispensed with, in which case monopotassic orthophosphate is obtained.

In this case there is added to the watery solution of the pyrophosphate of potassium, in which as above mentioned soluble metaphosphate of potassium may also be contained, so much phosphoric acid that 1 molecule of phosphoric acid to each molecule of potash is present in the fluid, which is afterwards boiled for several hours.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. The herein described process for converting insoluble metaphosphate of potassium into the soluble condition by
    (*a*) Melting the metaphosphate of potassium which is insoluble in water, and cooling the fused mass rapidly, by which means the fused material is prevented from passing into the crystalline condition, and soluble metaphosphate of potash is produced.
    (*b*) By fusing metaphosphate of potassium insoluble in water with chloride of potassium at a red heat in the presence of the vapour of water, whereby, as the result of the action of the water vapour upon the fused mixture, pyrophosphate of potassium soluble in water is produced.
2. The employment of the soluble metaphosphate or pyrophosphate of potassium obtained as described under (*a*) or (*b*) in Claim 1, for rendering insoluble phosphate of aluminium soluble in water by fusing the latter with metaphosphate or pyrophosphate of potassium or a mixture of the two.
3. The employment of the soluble phosphates of potassium obtained as described under (*a*) or (*b*) in Claim 1 for the production of orthophosphate of potassium.
    (*a*) By heating a watery solution of these salts under pressure.
    (*b*) By heating pyrophosphate of potassium obtained as described under (*b*) in Claim 1 (with which the soluble metaphosphate of potassium obtained as described under (*a*) in Claim 1 can be mixed) in a watery solution with so much phosphoric acid that 1 molecule of the latter is present to each

molecule of potash, whereupon the formation of monopotassic orthophosphate occurs.

Dated the 2nd day of January 1893.

G. F. REDFERN & Co.,
4, South Street, Finsbury, London, Agents for the Applicant.

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412 Translation of article from the periodical: Zeitschrift fur anorganische Chemie, vol. 65, 1910, pages 1 to 9 inclusive.

"The polyphosphates"

By

N. Parravano and G. Calcagni (1)
(with two figures in the text"

Fleitmann and Henneberg (2) in the year 1848 in the course of studies of Graham on the acids of phosphorus replaced the known scheme of Graham for the illustration of the various circumstances under which phosphoric acid anhydride combines with water by a new one in which 6 mol. water unite with successively increasing amounts of anhydride:

$$6H_2O + 2P_2O_5 = H_{12}P_4O_{16} = 4H_3PO_4$$
$$6H_2O + 2P_2O_5 = H_{12}P_6O_{21} = 3H_4P_2O_7$$
$$6H_2O + 4P_2O_5 = H_{12}P_8O_{26} = 2H_6P_4O_{13}$$
$$6H_2O + 5P_2O_5 = H_{12}P_{10}O_{31}$$
$$6H_2O + 6P_2O_5 = H_{12}P_{12}O_{36} = 12HPO_3$$

Therefore they inserted between phosphoric acid and metaphosphoric acid two new acids, one with 4 and one with 10 atoms of phosphorus which, like pyrophoric acid, may be regarded as composed of several molecules of phosphoric acid by the elimination of water:

$$4H_3PO_4 - 3H_2O = H_6P_4O_{13}$$
$$10H_3PO_4 - 9H_2O = H_{12}P_{10}O_{31}$$

The justification of this scheme F. and H. then sought to prove by an experimental examination of the possibility of existence of the two new acids. They succeeded on the one hand in producing some salts of the type of tetraphosphoric acid and on the other hand in obtaining an insoluble silver salt of the composition of a decaphosphate.

413 Further Gerhardt occupied himself with the tetraphosphates which he considered to be double salts of

neutral and acid pyrophosphate, and also Uelsmann (1) who made and analyzed the sodium and silver salts. Later only a little work has been done on polyphosphates; Schwarz (2) and Stange (3) have made salts which may be attributed to a new polyphosphoric acid, triphosphoric acid $H_5P_3O_{10}$, and even more recently one of us has published analyses (4) of a sodium polyphosphate which belongs to the next to the last member of the series of Fleitmann and Henneberg.

As is apparent the information on these compounds is comparatively defective. In the first place we do not know how many of them are capable of existence; if, as is the view today, we enumerate them as condensed phosphoric acids then the question arises of the condensation ability of phosphoric acid because Schwarz, apart from the above mentioned tri-,tetra- and decaphosphates, has called attention to the possibility of the existence of a compound $9Na_2O \cdot 5\ P_2O_5$. We do not know the true nature of these salts either. The authors who made them regarded them as salts of tri- and tetraphosphoric acid; however we can not say that they have furnished a proof of it. Tetraphosphoric acid according to Fleitmann and Henneberg is characterized by the insolubility of the magnesium salt which distinguishes it from metaphosphoric acid and by the solubility of the silver salt which distinguishes it from pyrophosphoric acid. The former statement is based on a single determination of magnesium in a precipitate which possibly as frequently happens in similar cases holds inclosed the sodium salt carried over from the reaction; the second statement is incorrect because as a matter of fact silver pyrophosphate is not at all soluble in an excess of
414 sodium pyrophosphate. Further as far as triphosphoric
acid is concerned Stange states, after describing numerous salts which are said to be derived from it, at the conclusion of his work that neither the amorphous nor the crystallized salts, which were made by him and Schwarz, could be used as a proof of the existence of tri-

phosphoric acid; this he does not see in the other facts which in reality are not more conclusive than those which he himself considers to be inadmissible.

Our knowledge concerning these salts is therefore a very defective one; this is in part also due to the difficulties which their investigation offers; analytical difficulties, because slight differences in the composition of the compound such as often occur in salts, which crystallize only with difficulty from sirupy solutions, frequently render difficult any decision as to whether we have to do with impurities with metaphosphate or with a mixture of various phosphates; further difficulties arise in the interpretation of the results in consequence of the tendency of the pyrophosphate and of the various polymeric forms of the metaphosphate to form double salts.

Therefore we considered it advisable to undertake new tests with the polyphosphates and to do so by a method different from those hitherto followed.

The polyphosphates may be regarded as products of the union of pyrophosphate with metaphosphate; there result the sodium salts:

$$Na_4P_2O_7 + NaPO_3 = Na_5P_3O_{10}$$
$$Na_4P_2O_2 + 2NaPO_3 = Na_6P_4O_{13}$$
$$Na_4P_2O_7 + 8NaPO_3 = Na_{12}P_{10}O_1$$

415 Actually we obtain by fusing pyrophosphate with metaphosphate in various proportions the different types of polyphosphates. Therefore we can determine the nature and number of the products which are formed in the union of the pyrophosphates with the metaphosphates by the study of the condition diagram of these two salts by means of thermal analysis (1).

The results of the thermal analysis are in general only conclusive if they turn out positively as the formation requirements of one compound may be different from the conditions under which the observation of the cooling curves of the mixtures is effected. On the other hand in the case of the polyphosphates the thermal analysis offered itself as a procedure which ought to have led directly to indisputable results as the formation requirements of the polyphosphates correspond throughout the conditions which are observed in the case of thermal analysis so that therefore all possible condensation products ought to have been discoverable.

We have therefore studied the fusion diagrams of the systems $K P O_3$ — $K_4P_2O_7$ and $Na P O_3$ — $Na_4P_2O_7$ and in particular we treated first the potassium salts because they both crystallize out well and have sharply distinct melting points. The salts were furnished by the firm of C. A. F. Kahlbaum. We always used 50 g. of the mixture pulverized as finely as possible which was melted in a platinum crucible in a Heraeous electric resistance furnace. The mixtures were all heated to 1100 to 1200°, that is, to a considerably higher temperature than necessary for complete fusion. They were kept for a considerable time at this high temperature before the cooling began. The cooling
416 took place in the same furnace while the upper opening of the same was carefully closed in order to avoid any draft.

For measuring the temperature we used a platinum—platinum + rhodium thermo- couple of the Heraeous type. The thermo- couple, protected by a tube of Marquardt porcelain dipped in the molten mass. The two wires of the thermo- couple were insulated from one another by a thin tube of difficultly fusible material. The ends of the thermocouple were connected by means of terminal screws with thick copper wires which led to the Siemens- galvanometer: the points of connection of the thermo- couple with the copper wires were kept at 0^0 by ice cooling.

The temperatures were read off on the scale of the galvanometer at $10''$ intervals and checked by determination of the melting points of copper and aluminum. The results obtained are combined in the following table.

The table gives the following diagram (fig. 1).

This is a diagram of two substances which give mixed crystals with a miscibility gap which extends from a concentation of 87 down to 9% of metaphosphate. The curves AB and BC give the composition of the fluid solutions from which at the temperatures of the corresponding ordinates begins the precipitation of the solid solution. The curves AD and CE indicated by dotted lines which would give the composition of the solid solutions in equilibrium with the fluid solutions indicated by the curves AB and BC.

417 **TABLE.**

KPO_3	$K_4P_2O_7$	Temp. at the beginning of the crystallization in degrees	eutectic temp. degrees	duration of eutectic holding point

we have not been able to determine experimentally because the speed of crystallization of the mixtures is too slight, so that the breaks on the cooling curves corresponding to complete solidification disappear.

The beginning of solidification as well as the eutectic crystallization is often retarded by supercooling; by vigorous stirring of the molten mass, however, this disadvantage can be avoided. The stirring is continued until the stirrer can no longer move in the almost solidified mass. The times of the eutectic holding point are given on the eutectic horizontal line. The concentrations of the saturated mixed crystals D and E lie at a content of 87% and 9% of metaphosphate respectively.

As is apparent, the diagram, contrary to our assumption, does not show the existence of compounds between KPO_3 and $K_4P_2O_7$. The triphosphate would correspond to a concentration of 26. 33%, the tetraphosphate to one of 41.68% KPO_3. With these concentrations there are no indications any more than in the others which might lead one to conclude the formation of compounds.

We now turned, as potassium polyphosphates were not obtained, to the study of the phase diagram $NaPO_3$ — $Na_4P_2O_7$. In doing so a difficulty is encountered. So-

418 dium metaphosphate is, as we may also obtain it by heating to the melting point, a vitreous mass. Consequently all mixtures with a considerable content of metaphosphate show this same vitreous nature and therefore are not to be considered in any discussion of the diagram because they regularly show holding points at temperatures which vary within an interval of 100 degrees and more. For this reason in the following table only data are given which relate to the primary separation of the pyrophosphates from the molten mixtures.

$NaPO_3$ %	$Na_4P_2O_7$ %	Temp. at beginning of crystallization in°.	Eutectic temp. in°.	Duration of eutectic holding point in seconds.

These figures are obtained from the diagram (fig. 2).

The test arrangement was in the instance of the investigation of the sodium salts in general the same as in that of the potassium salts with the single difference that the point where the thermo- couple was soldered was immersed directly without any protection by a porcelain tube in the molten mixture.

As we see, the diagram Na PO_3 — $Na_4P_2O_7$ is absolutely the same as that of the corresponding potassium salts in the sense that here too the formation of compounds is not apparent.

Now how can these negative results be harmonized with the doubtless sure and indisputable existence of the so-called polyphosphates? The results of the thermal analysis can, as we have already emphasized, only be decisive in the case where they turn out positive. If they are negative then they offer no evidence chiefly for two reasons: in
419 the first place the conditions of formation of the compounds may be different from those under which the thermal analysis was performed, and in the second place in the molten and solidifying masses metastable equilibriums might occur which are only upset with difficulty. But the conditions of formation of the polyphosphates are doubtless the same as those under which the

thermal analysis is performed. At any rate, the temperature might play a part to which the mixtures were heated for determining the cooling curves, under the assumption that similar phenomena occur here to those which take place in the case of alloys of antimony and aluminum (1) where the separation of the compounds is actually dependent on the temperature to which the mixtures are to be heated before cooling. The various authors who have made polyphosphates have, however, used a blower so as to be able to melt comparatively considerable quantities of the mixtures; therefore it is certain that they have in no case exceeded the temperatures which we attained in the electric furnace. The second assumption which we may make is that, as stated, metastable equilibriums occur in the polyphosphate melts which can not be avoided under the given test conditions. Treitschke (1) found in the investigation of alloys of antimony and cadmium that if the mixtures are allowed to cool without being stirred the melting curve will have a course for a certain concentration interval which varies if we stir and at a suitable time inoculate some of the same alloy; the solidification begins then at a higher temperature, a new compound crystallizes from the mixture and the melting curve has a different
course. In these alloys there may, therefore, be
420 metastable equilibriums which can be offset by stirring and inoculation.

In our case it might likewise be a question of such equilibriums as can not be offset under the test conditions observed. This possibility may be admitted; however we have, apart from the tests communicated here, which were carried out in the Heraeus furnace, also conducted numerous others, in all more than a hundred, in which not 50 but 100 g. of the mixtures were melted in the Perrot furnace. We allowed the mixtures to cool very quickly or very slowly, stirred the molten masses vigorously until the stirrer could no longer move in the almost completely solidified mixture, studied further an entire series of melting curves as far down as 200 and 150° and nevertheless could not determine the presence of any irregularities which might have pointed to other processes than those observed. If actually it had been a matter of metastable equilibriums then as a result of such a considerable number of tests some proof of their existence would certainly have been obtained.

In the case of sodium salts we have gone even farther. We made the sodium triphosphate and the sodium tetraphosphate and injected into the mixtures of suitable concentration at the proper time crystals of tri- and tetraphosphate. The results thus obtained were in no way distinguished from the earlier ones inasmuch as this inoculation in no way changed the course of the cooling curve.

If it is desired, therefore, in view of all these experiments, to regard the results of our tests as conclusive then, without excluding the possibility that the formation of
polyphosphates in our diagrams perhaps did not ap-
421 pear in consequence of very persistent metastable
conditions, we may make the following conclusion: the polyphosphates may be obtained from aqueous solutions but can not be formed in the melt composed of pyrophosphate and metaphosphate; we must assume then that for their formation the presence of water is necessary; however they can not be referred directly to the acids $H_6P_5O_{10}$ and $H_6P_4O_{13}$ for the existence of which there is still lacking according to our tests a valid demonstration.

422 Gmelin's "Handbuch der anorganischen Chemie",
8th Edition, Volume "Natrium", 1927, pages 924-925

Sodium polyphosphates

Parravano, Calcagni (Atti Linc. (5) 1 7 I (1908) 731; Z. anorg. Ch. 6 5 (1909) 1) form the fusion diagram of the system $Na_4P_2O_7$. Na P O_3 were not able to find any indications of the formation of compounds. On the other hand Fleitmann, Hennerberg (Lieb. Ann. 6 5 (1848) 324) and F. Schwarz (Z. anorg. Ch. 9 (1895) 253) obtained from the melt of $Na_4P_2O_7$ and $Na P O_3$ in definite proportions by lixiviation with water various crystallized polyphosphates. Completely satisfactory investigations as to whether it is a matter here of homogeneous compounds or of a mixture of different phosphates are not available.

$Na_5P_3O_{10}8$ (?) H_2O or 5 Na_2O .3P_2O_5.16 (?)H_2O. We heat a mixture of 100 g. of $Na_4P_2O_7$ and 50 to 55 g. hexametaphosphate to the melting point and obtain by stirring for some time in the flux. After slow cooling the cooled melt is broken into individual pieces, then treated with cold water and allowed to stand over night. The filtered solution is made to crystallize by voluntary evaporation and the salt of the above substance separates in the form of four sided right angled laminae, probably belonging to the
triclinic system. The content of water varies some-
423 what but probably amounts to 8 H_2O. The salt is
very soluble in water and reacts slightly alkaline even
after lengthy heating, F. Schwarz (Z. anorg. Ch. 9 (1895) 253), Stange (Z. anorg. Ch. 1 2 (1896) 445). On the heating of its aqueous solution it decomposes completely into its components: pyro-and metaphosphate. By $N H_3$ according to F. Schwarz (see above) conversion into orthophosphate is effected: Stange (see above) could not confirm this conversion. According to both authors it is not a matter here of a double salt but of the sodium salt of triphosphoric acid $H_5P_3O_{10}$.

$Na_6P_4O_{13}$. 18 H_2O or 6 Na_2O. 4 P_2O_5. 36 H_2O. We heat a mixture of 76.9 parts of hexametaphosphate with 100 parts $Na_4P_2O_7$ or one of 187.3 parts $(Na P O_3)_6$ with 100 parts $Na_3P O_4$ in the platinum crucible until the melting point and keep in fluid state (flux) for some time by stirring. If the cooled, white, crystalline mass is triturated as fine as possible, then an amount of hot water not sufficient for solution poured over it and if after cooling it is filtered then there will be formed on standing for 12 to 24 hours crystals of the hyrdous salt of the above substance in delicate thin laminae, Fleitmann, Hennerberg (Lieb. Ann. 6 5)

1848 324). Uelsmann (Lieb. Ann. 1 1 8 (1861) 100), F. Schwarz (Z. anorg. Ch. 9 (1895) 252). See also Salzer (Arch. Pharm. 2 3 2 (1894) 370). The salt loses its water of crystallization over H_2SO_4 or at 100°, Uelsmann (which see). It dissolves in about 2 parts of cold water; the solution reacts slightly alkaline but after a brief heating
424 shows an acid reaction, Fleitmann, Hennerberg (which see).

The anhydrous $Na_6P_4O_{12}$ is obtained by heating $Na_3HP_2O_7 \cdot H_2O$ to 300°, Partington, Wallsom (Chem. N 1 3 6 (1928) 98).

$Na_{12}P_{10}O_{31}$ or $6\ Na_2O.\ 5\ P_2O_5$ If obtained by melting together 100 parts $Na_4P_2O_7$ with 307.5 parts $(NaPO_3)_6$. The compound crystallizes still more difficultly than $Na_6P_4O_{13} \cdot 18\ H_2O$; after the melting we have a vitreous mass, Fleitmann, Hennerberg (Lieb. Ann. 6 5 (1848) 333).

$Na_4P_6O_7$ or $6\ Na_2O.\ 9\ P_2O_5$ This salt is easily obtained by evaporation of solutions of $NaOH$ or Na_2CO_3 and P_2O_5 and heating to a bright red glow. When fused it is a vitreous mass which dissolves slowly in cold water, more rapidly in hot water and reacts almost neutral to methyl orange and phenolphthalein. When its aqueous solution is heated it will be broken up into metaphosphate and free H_3PO_4 not HPO_3. On being heated with excess mineral acid there will be found in the solution finally only H_3PO_4. The salt has a strongly corrosive action on glass, porcelain, SiO_2, Pt and Ni which also prevented an exact determination of the composition of the salt, J. H. Smith (J. Soc. chem. Ind. 3 6 (1917) 419).

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427 *Examiner's Statement.*

This is an appeal from the action of the Primary Examiner finally rejecting Claims 3, 4, 9 to 14 and 20 to 54. Claims 1, 2, 5 to 8 and 15 to 19 have been cancelled. No claims have been allowed. Applicant submits an amendment with the appeal in which he proposes to substitute

Claims 62 to 69 for Claims 3, 4, 9 to 14, 20 to 33 and 40 to 54. This amendment, along with the affidavit accompanying it, have been entered for purposes of appeal thus leaving for consideration Claims 34 to 39 and 62 to 69.

The appealed claims are as follows:

34. A process which comprises adding to hard water a water soluble salt or tetraphosphoric acid, $H_6P_4O_{13}$, so as to combine with an alkaline earth metal to prevent the deposition of an alkali earth metal compound therein.

35. A process which comprises adding to hard water a water soluble salt of tetra phosphoric acid, $H_6P_4O_{13}$, so as to combine with calcium to prevent the deposition of a calcium compound therein.

36. A process of softening water, which comprises decreasing the free ion concentration of an alkaline earth metal in hard water with a water soluble salt of tetra phosphoric acid, $H_6P_4O_{13}$.

37. A process of softening water which comprises decreasing the free ion concentration of an alkali earth metal in hard water with an alkali metal salt of tetraphosphoric acid, $H_6P_4O_{13}$.

428 A process of softening water which comprises decreasing the free ion concentration of calcium in hard water with a water, soluble salt of tetraphosphoric acid, $H_6P_4O_{13}$.

39. A process of softening water which comprises decreasing the free ion concentration of calcium in hard water with an alkali metal salt of tetraphosphoric acid, $H_6P_4O_{13}$.

62. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein to prevent deposition of said compounds therein, the water soluble heat reaction product of sodium metaphosphate and tetrasodium pyrophosphate to produce when dissolved in water an aqueous solution thereof having a pH between 8 and 10, the weight proportions of sodium metaphosphate and tetrasodium pyrophosphate in said reaction product falling within the range of 50:50 and

20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium meta and tetrasodium pyrophosphate.

63. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein, to prevent deposition of said compound, the heat reaction product of monosodium and disodium orthophosphate, to produce when dissolved in water an aqueous solution having a pH between 8 and 10, the weight proportions of $NaPO_3$, derived from said monosodium orthophosphate, and $Na_4P_2O_7$, derived from disodium orthophosphate in said reaction product, falling within the range of 50:50 and 20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium metophosphate and tetrasodium pyrophosphate.

64. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein to prevent deposition of said compound, the heat reaction product of monosodium and disodium orthophosphate, to produce when dissolved in water, an aqueous solution having a pH between 9 and 10, the molecular proportions of $NaPO_3$ derived from monosodium orthophosphate, and $Na_4P_2O_7$ derived from disodium orthophosphate in said heat reaction product being substantially 1 to 1, said heat reaction product being further characterized in
429 that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.

65. A process which comprises adding to hard water, so as to combine within alkaline earth metal compound therein to prevent deposition of said compounds, the water soluble heat reaction product of soda ash and orthophos-

phoric acid, to produce when dissolved in water an aqueous solution thereof having a pH between 8 and 10, the theoretical weight proportion of sodium metaphosphate and tetrasodium pyrophosphate in said reaction product falling within the range of 50:50 and 20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.

66. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein to prevent deposition of said compound, the water soluble heat reaction product of soda ash and orthophosphoric acid to produce when dissolved in water an aqueous solution thereof having a pH between 7 and 10, the theoretical weight proportion of sodium metaphosphate and tetrasodium pyrophosphate in said reaction product falling within the range 20:80 and 80:20 respectively, said heat reaction product containing a proportion of sodium acid pyrophosphate, and being characterized further in that its power to prevent deposition of said alkaline earth metal compounds is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.

67. The process which comprises softening a hard water by adding to said hard water sodium triphosphate $Na_5P_3O_{10}$.

68. The process which comprises softening a hard water by adding to said hard water a composition comprising the compound sodium triphosphate, $Na_5P_3O_{10}$, to prevent the deposition of an alkaline earth metal compound in said water.

69. A process which comprises adding to hard water a water-soluble polyphosphate so as to combine with an alkaline earth metal to prevent the deposition of an alkaline earth metal compound therein.

430 The references relied on are:

Hall, 1,903,041, March 28, 1933, 210/23

Hall, 1,956,515, April 24, 1934, 210/23

Precht (Br.), 7,958, April 27, 1892, 23/106

Precht, 502,424, Aug. 1, 1893, 23/106

Tanner, 123,743, Feb. 13, 1872, 23/107

Gmelin's Handbuch 8th Edition, Vol. Sodium, 1927, pages 924-5.

The Polyphosphates—N. Parravano, G. Calcagni.

Zeitschrift fur Anorganische Chemie, Vol. 65, 1910, pages 1-9.

Applicant's alleged invention relates to dehydrated phosphates of sodium and to a process for producing such phosphates. Applicant recites as an object of the invention the provision of an improved water softening and scale inhibiting compound which shall have a predetermined hydrogen ion concentration in its aqueous solution and which shall have pronounced buffering properties in such solution. Applicant on pages 1 and 2 says, "In some cases it is desirable to employ as a water treating agent pyro and meta phosphates which will give the desired alkalinity to boiler water and at the same time exhibit a delayed precipitating action towards the alkaline earth metal salts present in natural waters. The pyro and meta phosphates are especially well suited for this purpose, since they do not immediately hydrate to the ortho-phosphates and hence do not immediately precipitate insoluble ortho-phosphates. For some purposes a greater delay in the rapidity of the reversion of such meta or pyrophosphates to the orthohosphates is desirable and it is a further additional object of the present invention to provide a dehydrated phosphate product, which exhibits an increased resistance to reversion. We have found that mixtures of tetrasodium pyrophosphate and sodium meta-
phosphate fused together and chilled to form an
431 amorphous glass-like soluble dehydrated phosphate
product are particularly suitable for the present purpose. By varying the constituents of the product any desired hydrogen ion concentration between the limits of ph=6.$_4$ to pH=10.2 may be obtained. We have furthermore found that readily soluble mixtures of molecularly

dehydrated sodium phosphates of a predetermined hydrogen ion concentration may be obtained by heating to the fusion point appropriately proportioned mixtures of sodium ortho-phosphates, or mixtures of ortho-phosphoric acid and the sodium salt of a replaceable acid and then rapidly cooling. Suitable sodium salts for this purpose are the chloride and carbonate of sodium, although others may be used.”

Applicant gives two examples illustrating methods of preparing the compounds in question. In example 1, 76.5 lbs. of mono-sodium ortho-phosphate ($NaH_2PO_4.2H_2O$) and 134.7 lbs. of di-sodium ortho-phosphate ($Na_2H\ PO_4.12H_2O$) are mixed together, dehydrated and heated to the melting point of the mixture which is at a temperature of approximately 620°C. When a uniform melt has been obtained it is quickly cooled by pouring it on a cold metal surface in thin layers. This, according to applicant, results in approximately 100 lbs. of a solid consisting theoretically of 50 per cent tetrasodium pyro-phosphate and 50 per cent sodium meta-phosphate and when dissolved in water to make a 1 per cent solution will show a pH of approximately 8.6. The reactions for stoichiometrically determining the theoretical proportions in this example are given as follows:

432

$$NaH_2PO_4\ .\ 2H_2O = Na\ PO_3 + 3H_2O$$
$$2(Na_2HPO_4\ .\ 12H_2O) = Na_4P_2O_7 + 25H_2O$$

In example 2, 74.14 lbs. of sodium carbonate (soda ash) and 78.26 lbs. of phosphoric acid, H_3PO_4 (or 104.2 lbs. of 75% H_3PO_4) are mixed together, heated slowly as long as carbon dioxide and water vapor are evolved, heated gradually to the melting point which is at a temperature of approximately 940°C. and then quickly cooled. Approximately 100 pounds of a mixture having a theoretical composition consisting of 80% tetra sodium pyrophosphate and 20% of sodium metaphosphate will be obtained. A sample of this material dissolved in water so as to make a 1% solution will show a pH in the neighborhood of 9.5. The reactions for stoichiometrically determining the theoretical proportions in this example are:

$$Na_2CO_3 + 2H_3PO_4 = 2Ha\ PO_3 + CO_2 + 3H_2)$$
$$2Na_2CO_3 + 2H_3PO_4 = Na_4P_2O_7 + 2CO_2 + 3H_2O$$

The patent to Hall 1,903,041 relates to water treatment and particularly to the treatment of steam boiler water with chemicals whose aqueous solutions are either alkaline or of relatively slight acidity but which through changes wrought in their character at the temperatures and under the conditions obtaining in the boiling water undergo transformation which increases their alkali-neutralizing capacity. The chemicals used by the patentee are sodium metaphosphate and/or sodium pyrophosphate. It is emphasized throughout the specification that a desirable alkalinity for the boiler water is around a pH of 9 or 10 or even higher.

433 The patent to Hall 1,956,515 relates to water softening and washing and more particularly to the softening of water by the use of an alkali-metal metaphosphate. Hall's preferred material is the soluble sodium metaphosphate sometimes called "Graham's salt", which may have mixed with it a small amount of sodium pyrophosphate. Graham's salt is believed to consist principally of sodium hexametaphosphate. The sodium hexametaphosphate in readily soluble form may be prepared by strongly heating monosodium dihydrogen orthophosphate and rapidly cooling the molten mass. In order to form a water softener which is substantially netural Hall adds a small amount of sodium carbonate to the monosodium dihydrogen orthophosphate at the time of fusion, this addition resulting in the presence of an equivalent amount of sodium pyrophosphate in the fused product. The amount of sodium carbonate used will determine the neutrality or slight alkalinity of the fused product.

The British patent to Precht relates to a process for producing phosphates of potassium which are soluble in water. The process may be carried out by (1) melting the metaphosphate of potassium which is insoluble in water and

cooling the fused mass rapidly or (2) by fusing metaphosphate of potassium insoluble in water with chloride of potassium at a red heat in the presence of the vapor of water. Or as pointed out on page 2, lines 29 to 32 a phosphate of potassium which is perfectly soluble in water is formed if one
molecule of phosphoric acid and one molecule of pot-
434 ash (K_2CO_3) or if at least 66.2 parts by weight of the
latter to 100 parts of anhydrous phosphoric acid are
present in the fused mass. It is further stated in lines 32 to 35 that in practice it is advantageous to work with a larger proportion of potash, so that the phosphoric acid in the fused mass is present partly in the condition of pyrophosphate of potassium.

The U. S. patent to Precht teaches the same process as the British patent to Precht explained above.

The patent to Tanner relates to a process for manufacturing the phosphates of the alkalies. Phosphoric acid is mixed with chloride of sodium and subjected to heat to produce what the patentee terms monosodic phosphate. By varying the proportions of the starting materials other phosphates may be produced.

Gmelin's "Handbuch der Anorganischen Chemie", 8th Edition, Volume "Natrium", 1927, pages 924-925, discloses the polyphosphates such as sodium triphosphate and sodium tetraphosphate and methods for producing these polyphosphates.

The article from Zeitschrift fur Anorganische Chemie, Vol. 65, 1910, pages 1 to 9 inclusive, deals with the polyphosphates and mentions among others sodium triphosphate and sodium tetraphosphate.

Claims 34 to 39, inclusive, were finally rejected under the provisions of Rule 132 in accordance with the decision of the Board of Appeals in interference No. 73850 affirming the action of the Primary Examiner in granting a motion to dissolve on the ground that Durgin could not make the
claims of the interference since they included matter
435 which had no proper basis in his original specifica-

tion. At no place in the specification is there any mention of an alkali metal tetraphosphate for use in the softening of water. In further explanation of the above rejection it may be pointed out that these claims were copied from patent No. 2,059,570 issued Nov. 3, 1936 to Augustus H. Fiske et al and correspond to Claims 1 to 6 thereof. An interference was declared and a motion to dissolve filed by Fiske et al, said motion being based on the ground that Durgin et al could not make the counts since he did not disclose a tetraphosphate or a process of manufacture which would necessarily result in the formation of such. This motion was granted and the interference dissolved. On appeal the Examiner was affirmed by the Board of Appeals. Durgin is again submitting these claims for consideration by the Board of Appeals in view of additional facts in affidavit form which applicant contends could not have been submitted under the Rules of Practice, during the hearing upon the motion. The authority cited was Horton vs. Leonard 1910 C. D. 81 although it is pointed out that this case was somewhat different from the instant case in that the affidavit in question there was in support of a motion to dissolve on the ground of inoperativeness wherein here the affidavit would have been against a motion to dissolve on the ground that one of the parties could not make the claims. It is not clear therefore that Horton vs. Leonard is controlling in the present case and no good and sufficient reason is seen why the affidavits of Clarke and Miles were not presented for consideration by the Board of Appeals in the previous appeal on these claims.

436 Applicant's affidavit submitted with the amendment of Oct. 20, 1939 will first be discussed in connection with the alleged formation of sodium tetraphosphate. Experiments A and E use the same starting materials as Examples 1 and 2 of Durgin but in different proportions. Since the relative proportions of the starting materials used determines the composition of the resulting product it does not appear that the products obtained from Examples 1 and 2

of Durgin will be the same as the products obtained from experiments A and E of the affidavit. Hence even assuming that the products obtained in experiments A and E of the affidavit are sodium tetraphosphate it does not appear that the products obtained from examples 1 and 2 of Durgin will also be tetraphosphates. Furthermore, in experiment A the materials are fused at a temperature of 950° C. while in Example 1 the materials are fused at a temperature of 620° C. The above comparisons are given to show that Durgin's original disclosure did not embrace the formation of any particular compound or compounds and in fact did not even recognize the formation of the polyphosphates as such or of the formation of different compounds. Applicant seemed to be concerned primarily with the formation of a phosphatic compound or mixture of such compounds which would have a predetermined hydrogen ion concentration in aqueous solution. It is true that applicant has a broad disclosure of varying the proportions of the starting materials but this apparently was for the purpose of varying the hydrogen ion concentration and not to form different compounds and hence is not considered a sufficient basis for the claiming of specific compounds. It further is not
437 clear whether applicant forms any particular polyphosphate or whether he forms a mixture of different phosphates. Admittedly there is some ortho and acid pyrophosphate present in the resulting product. See page 5, lines 18 to 29. Although the results of tests A to E tend to show the similarity of the compounds formed it is not conclusive that they are identical. The per cent P_2O_5 in the product depends of course upon the amount and proportions of the starting materials and it is believed that the other characteristics could conceivably be true of two or more closely related polyphosphates. However, even if we assume that the products of experiments A to E are the same applicant still has not established the identity with these products of the products of examples 1 and 2.

Claims 67 to 69 are rejected as including new matter for reasons as pointed out in the rejection of Claims 34 to 39.

Applicant has no disclosure of a triphosphate or even a polyphosphate as such. In order to establish the formation of sodium triphosphate applicant submits the affidavit of George L. Clark which contains X-Ray patterns of three samples of sodium polyphosphates. Sample 3 was said to be made according to example 2 of application #733,392. Two differences however are pointed out, one being that different proportions of the starting materials are used and the other being that the mixture is fused at about 1150° C rather than 940° C. Sample No. 4 is said to be sodium triphosphate made in accordance with the teaching of Andress and Wust. Sample No. 5 is said to be made in accordance with Example No. 2 of application #733392. 438

A study of the X-Ray patterns on page 2 of the affidavit of George L. Clark shows that No. 4 has a different appearance from Nos. 3 and 5. This difference has not been explained and leaves some doubt, in the Examiner's mind at least, as to the conclusiveness of the formation of identical compounds. In any event, as pointed out above in connection with Claims 34 to 39, it is not believed that applicant's original disclosure is sufficient to support claims drawn specifically to sodium triphosphate or even to a polyphosphate.

Claims 34 to 39 and 62 to 69 are rejected as unpatentable over Gmelin or Parravano and Calcagni in view of Hall. The water soluble heat reaction product of sodium metaphosphate and tetrasodium pyrophosphate including specifically sodium triphosphate and sodium tetraphosphate are all disclosed by Gmelin and Parravano. As regards the recitation of the heat reaction product of monosodium and disodium orthophosphate and of soda ash and orthophosphoric acid the use of these compounds merely moves the reaction back one step in that in each case the starting compounds are converted first into metaphosphate and pyrophosphate which are the starting materials of Gmelin and Parravano. The Hall patents relate to the treatment of water with phosphates which act in the same manner as

claimed for applicant's phosphates. Further, in carrying out the process of the Hall patent 1,956,515 wherein monosodium dihydrogen orthophosphate is mixed with sodium carbonate, fused and then quickly cooled it is conceivable that a portion of the resulting product would be in the
439 form of polyphosphate. In view of Hall no invention would be involved in utilizing the polyphosphates disclosed by Gmelin and Parravano for softening water. Applicant argues that since patent No. 1,956,515 to Hall was not filed until some three years after applicant's original application No. 438,955 was filed that the Hall patent is not a proper reference against the claims. It is pointed out however, that as originally filed application No. 438,955 contained no disclosure of utilizing the compounds there mentioned for the purpose of softening water and that such disclosure was not added to the application until the amendment of January 2, 1934, was filed. It therefore appears that as regards the use of the compounds disclosed for the purpose of softening water the Hall patent No. 1,956,515 antedates such disclosure by several months and is therefore a valid reference to show such use. Applicant further argues that the only difference between Hall patents No. 1,903,041 and 1,956,515 is that the latter additionally discloses water softening. If this is true it would seem to follow that the results produced in the practice of the process of patent No. 1,903,041 would inherently be the same as the results produced in the practice of the process of patent No. 1,956,515 although not recognized in the earlier patent. In any event the earlier Hall patent does disclose the use to the same extent as originally disclosed by applicant in application No. 438,955 and to that extent is pertinent.

The claims are further rejected on Hall in view of Precht and Tanner. Claims 62 to 66 in particular call for
440 the heat reaction product of certain phosphatic compounds. Tanner discloses the mixing of phosphoric acid with sodium chloride and heating which is the equivalent of the soda ash and orthophosphoric acid called for by Claims 65 and 66. The patents to Precht disclose the for-

mation of potassium phosphates which are considered the equivalent of the sodium phosphates as called for by the claims. Hall et al refers to polymerized forms of sodium metaphosphate and discloses the fusing together of monosodium di-hydrogen phosphate and sodium carbonate. Hall furthermore discloses a mixture of sodium metaphosphate and sodium pyrophosphate which would meet the terms of Claims 62 to 66 in that the heat reaction product of the various compounds mentioned might be nothing more than a mixture of sodium metaphosphate and sodium pyrophosphate.

It is further pointed out in connection with Claims 62 to 66 that there is not a sufficient basis in the original specification to support the range of weight proportions or molecular proportions of $NaPO_3$ and $Na_4P_2O_7$ recited:

In summary it may be stated that Claims 34 to 39 reciting the tetraphosphate, Claims 67 and 68 reciting the triphosphate, and Claim 69 reciting the polyphosphate have no sufficient basis in the original specification and that these claims are unpatentable over the cited art which discloses the particular compounds as well as the same use of analogous compounds; that Claims 62 to 66 reciting a heat reaction product of certain phosphates involve nothing more than mixtures of meta and pyrophosphate and are
441 clearly unpatentable over Hall who discloses the same mixture for the same use, Gmelin or Parravano who disclose the mixture and either Precht or Tanner who disclose similar mixtures or compounds.

Respectfully,

E. L. SHEFFIELD,
Examiner, Div. 49.

This statement was mailed to the attorney and returned by him in exchange for a duplicate carbon copy.

E. L. SHEFFIELD,
Ex. Div. 49.

* * * * * * * * * *

442 *Examiner's Supplementary Statement.*

The application identified above was remanded to the Primary Examiner to make such disposition of the amendment and affidavits filed December 14, 1940 as the Examiner deems proper.

Since applicant has not even attempted to explain why the amendment and affidavits were not presented before the final rejection was made or before or at the time the appeal was taken the amendment and affidavits are refused entry and consideration.

Moreover, it appears the affidavits, if pertinent to applicants' right to make claims 34 to 39, should have been presented while Interference No. 73,850 was pending. If Claims 34 to 39 were allowed to applicant it would be necessary to redeclare the interference.

Respectfully,

E. L. SHEFFIELD,
Examiner, Div. 49.

443 Endorsed: U. S. Patent Office Board of Appeals
Apr. 21, 1941 Mailed

Appeal No. 33,063 Paper No. 47
Hearing: April 2, 1941 RHJ

In the United States Patent Office

Before the Board of Appeals

Ex parte C. B. Durgin, R. N. Foster and C. F. Booth

Application for Patent filed July 2, 1934, Serial No. 733,392.

Soluble Dehydrated Sodium Phosphates and Process for Producing Same.

Mr. Herbert J. Krase and Mr. J. R. Wilson for appellants.

This is an appeal from the action of the Primary Examiner finally rejecting claims 34 to 39 and 62 to 69.

Claims 34, 62 and 67 will serve as illustrative:

34. A process which comprises adding to hard water a water soluble salt of tetraphosphoric acid, $H_6P_4O_{13}$, so as to combine with an alkaline earth metal to prevent the deposition of an alkali earth metal compound therein.

62. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound therein to prevent deposition of said compounds therein, the water soluble heat reaction product of sodium metaphosphate and tetrasodium pyrophosphate to produce when dissolved in water an aqueous solution thereof having a pH between 8 and 10, the weight proportions of sodium metaphosphate and tetrasodium pyrophosphate in said reaction product falling within the range of 50:50 and 20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium meta and tetra sodium pyrophosphate. 444

67. The process which comprises softening a hard water by adding to said hard water sodium triphosphate, $Na_5P_3O_{10}$.

The references relied upon by the examiner are:

Tanner,	123,743,	Feb. 13, 1872,
Precht (Br.),	7,958,	Feb. 25, 1893,
Precht,	502,424,	Aug. 1, 1893,
Hall et al,	1,903,041,	Mar. 28, 1933,
Hall,	1,956,515,	Apr. 25, 1934,

The Polyphosphates, N. Parravano, G. Calcagni, Zeitschrift Fur Anorganische Chemie, Vol. 65 (1910) pp. 1 to 9,

Gmelins Handbuch, 8th Ed., Vol. Sodium (1927) pp. 924-5.

The claims on appeal are directed to a process of treating water for softening or scale-prevention purposes which involves adding to the water a phosphate salt of sodium which is variously defined as being a water soluble salt of tetraphosphoric acid, sodium triphosphate and a salt produced by the heat reaction of certain sodium- and phosphorus-containing compounds in specified proportions.

The claims which are directed to the use of a soluble salt of tetraphosphoric acid were considered by us in connection with an appeal filed by appellant in Interference No. 73,850. That interference was dissolved by the Primary Examiner on the ground that appellant was not entitled to make the counts thereof which were copied from a patent to Fiske et al. The examiner's holding with respect to appellant's right to make the counts was affirmed by the Board of Appeals.

The appeal as to claims 34 to 39 in effect involves
445 a reconsideration of our former holding with respect
to appellant's right to make these claims.

Admittedly, there is no definite teaching in this application as filed with respect to the use of water-soluble salts of tetraphosphoric acid for water-softening purposes nor for any other purpose. The application does teach that certain reaction products resulting from the fusion of phosphorus- and sodium-containing materials can be used for water-softening purposes. It is appellant's contention that these reaction products inherently respond to the requirements of the claims of this group. As we pointed out in our former decision, it is possible that appellant's reaction products may contain a water-soluble salt of tetraphosphoric acid but it is also possible that the reaction product disclosed may not contain such material. Under such circumstances, a holding of necessary inherency cannot be made and it follows that appellant is not entitled to the claims.

In the application as filed, two examples are given: In the first, monosodium ortho-phosphate and disodium ortho-

phosphate are reacted at temperatures of approximately 620°. The product obtained from that reaction is described as "consisting theoretically of 50% tetrasodium pyrophosphate and 50% sodium metaphosphate. The reactants are so proportioned in initiating the reaction as to produce the proportions of pyrophosphate and metaphosphate
446 above referred to. In the second example, phosphoric acid and sodium carbonate are the reactants and the amounts thereof are stoichiometrically determined by the theoretical proportions necessary to produce a composition consisting of 80% tetrasodium pyrophosphate and 20% of sodium metaphosphate.

Appellant recognized that his reaction mixture was probably made up of substances other than the pyrophosphate and metaphosphate, with respect to which the reacting chemicals were originally chosen, but at no place does he disclose what the specific constituents of the resultant reacted mixture were. Certainly, the materials reacted were not stoichiometrically proportioned to produce the specific materials now claimed. According to the brief, the production of such materials requires a rather definite proportioning of the reactants and a rather definite reaction temperature. It may be, also, that definite proportions of water are required to give the precise materials here claimed. This seems to be supported by the Parravano et al treatise referred to by the Primary Examiner. According to the table given on the first page of the translation of this treatise, the production of tetraphosphoric acid requires the theoretical presence of 6 molecules of water to 4 molecules of phosphoric acid, P_2O_5. At any rate, we are not satisfied that there is any sufficient basis in this application as filed to warrant the allowance of claims directed either to water-soluble salts of sodium tetraphosphoric acid or sodium triphosphate.

447 Claims 62 to 66 are directed to a process which involves using a heat reaction product which is defined as having been made by appellant's disclosed procedure.

This material is also referred to as having a pH value within a certain range and a greater power to prevent deposition of alkaline earth material in the water being treated then an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate in like proportions.

The examiner has rejected the claims of this group on prior art which discloses the use of mixtures of metaphosphate and pyrophosphate for water-softening purposes and which also shows that it was known that sodium tetraphosphate and sodium triphosphate could be produced by fusing together suitable amounts of sodium meta phosphate and tetrasodium pyrophosphate. We are not satisfied that the substitution of these fusion products for mere mixtures of the starting materials from which such reaction products were produced was an obvious procedure, especially as the fused product appears to be considerably more efficient than the mixture itself.

Claims 62, 63 and 65 cover the use of a range of reactants capable of producing a sodium triphosphate and tetra sodium ortho-phosphate within the range of 50:50 and 20:80, respectively, whereas claim 64 covers only the 1:1 ratio. Claim 66 covers the broader ratio of from 20:80 to 80:20.

We think it a fair inference from the specification
448 that appellant rather carefully investigated the whole
field from 0:100 to 100:0. The examples given cover the specific and intermediate ranges recited but not the broader range of claim 66. However, we do not feel that there is any lack of basis for claims directed to these ranges of materials. We do feel, however, that the claims should be definitely limited in such a manner as to exclude mere mixtures of sodium metaphosphate and tetra sodium pyrophosphate such as are disclosed in the prior art. To this end we recommend the allowance of claims 62 to 66, if promptly amended as proposed in the communication filed December 14, 1940.

The Examiner's action is affirmed as to claims 34 to 49 inclusive, 67, 68 and 69, but is reversed with respect to claims 62 to 66 inclusive, subject to the authorized amendment above referred to.

BOARD OF APPEALS
W L REDROW
Examiner-in-Chief

W. L. THURBER
Examiner-in-Chief

B B PIERCE
Examiner-in-Chief

MR. J. R. WILSON
1700 S. Second St.
St. Louis
Mo.

449 *On Request for Correction of Typographical Error*

Our attention has been called to the fact that the expression, "tetra sodium ortho-phosphate" used in line 3 of the third paragraph of page 5 of our decision is apparently a typographical error as no such compound exists. Our statement with respect to claims 62, 63 and 65 was intended to follow, more or less, the language used in the last-mentioned claim. The term, "tetra sodium ortho-phosphate" should read, tetra sodium pyro-phosphate.

We note, also, that the term "sodium triphosphate" in the preceding line should have been sodium metaphosphate to agree with the corresponding terms used in the claims in question.

450 Our decision should be read as corrected.

BOARD OF APPEALS

W L REDROW
Examiner-in-Chief

W. L. THURBER
Examiner-in-Chief

B B PIERCE
Examiner-in-Chief

MR. J. R. WILSON
1700 S. Second St.
St. Louis
Mo.
May 5, 1941.

451 *On Request for Amendment of Decision*

In our decision of April 21, 1941, we made reference, in the third paragraph of page 5, to the use of a range of reactants capable of producing certain materials which were improperly named.

Our attention was called to this apparent inaccuracy which we attempted to correct by our supplemental decision of May 5, 1941. In this correction we stated that our original statement with respect to claims 62, 63 and 65 was intended to follow, more or less, the language used in the last-mentioned claim. Our attention is now called to the fact that, as applied to the claim first mentioned, the langguage is not now accurate as the original reactants are the materials which are now stated to be those which the
452 reactants are capable of producing.

As the petitioners note, in claim 62 the materials originally treated are sodium metaphosphate and tetra sodium pyrophosphate. It does not definitely appear, either in the claim or in the specification as filed that the final product is chemically different than the materials originally treated. It does appear that, by the treatment, these materials are in some way rendered more effective for their intended purpose.

Our original decision should be read with this correction, as well as the one made May 5, 1941, in mind.

BOARD OF APPEALS

W L REDROW
Examiner-in-Chief

W. L. THURBER
Examiner-in-Chief

B B PIERCE
Examiner-in-Chief

MR. J. R. WILSON
1700 S. Second St.
St. Louis
Mo.

May 28, 1941

* * * * * * * * * *

57 *Memorandum by the Court*

After careful consideration, the Court is unable to find that the position taken by the Patent Office was irrational or inconsistent with the evidence adduced at the hearing before this Court. The charts and test samples testified about by the Witness Reynolds, in the opinion of the Court, do not foreclose the conclusion, that from the known availability of metaphosphate and pyrophosphate salts of alkali earth metals for water-softening purposes, the intermediate triphosphate and tetraphosphate salts might also suggest themselves as an appropriate agent to one skilled in the art. If this is so, then the experimentation carried on by applicants was that of the routineer.

It is concluded that complainant's bill should be dismissed and counsel for defendant is requested to submit findings of fact and conclusions of law for resolution by the Court.

Done this 4th day of December.

EDWARD C. EICHER,
Chief Justice.

Copies sent to Attorney H. T. Stowell and Attorney W. W. Cochran.

* * * * * * * * * *

58 *Findings of Fact*

1. This is an action under R. S. 4915 (U. S. C. title 35, sec. 63) in which it was sought to have the Court find that the plaintiffs, Monsanto Chemical Company, Charles B. Durgin, Robert N. Foster and Charles F. Booth are entited to have issued to them a patent containing claims 34 to 39, inclusive, 67, 68 and 69 of application No. 733,392, of which application the Monsanto Chemical Company is assignee of the entire interest and the remaining three plaintiffs are the applicants.

2. At the trial the plaintiffs discontinued the action as to claim 69.

3. The application here involved relates to the softening of water and discloses the use of fused re-action products of pyro and meta phosphates as treating agents. In one specific example given, monosodium orthophosphate and disodium orthophosphate are reacted at about 620°C.
59 in another example phosphoric acid and sodium carbonate are the reactants. The application contains no express mention of the use of tetraphosphates or triphosphates for the softening of water.

4. Each of claims 34 to 39, inclusive, here involved, calls for use of a salt of tetraphosphoric acid for softening water and each of claims 67 and 68 calls for the use of sodium triphosphate for this purpose.

5. The plaintiff's application here involved did not, as filed, contain a disclosure of the use of a salt of tetraphos-

phoric acid, or of sodium triphosphate for the softening of water.

6. The plaintiff's application, as filed, did not contain a proper basis for claims 34 to 39, inclusive, 67 and 68, or any of them.

7. Claims 34 to 39, inclusive, 67 and 68 of plaintiff's application involve new matter and are, therefore, unpatentable.

8. The patent to Hall et al, No. 1,903,041, discloses the use of alkali-metal pyrophosphates and metaphosphates for the treatment of water.

9. The patent to Hall, No. 1,956,515, discloses the use of sodium metaphosphate, pyrophosphate or hexametaphosphate for the softening of water.

10. The eighth edition of Gmelin's Handbuch, Volume, Sodium, 1927, discloses on pages 924 and 925 the substances sodium tetraphosphate and sodium triphosphate, and methods of preparing them.

60 11. The article on pages 1 to 9 of the Zeitschrift fur Anorganische Chemie, Vol. 65, 1910, discloses alkali metal triphosphates and tetraphosphates, and methods of preparing them.

12. It would not require invention, in view of the Hall patent No. 1,956,515, or the Hall et al patent No. 1,903,041, and in view of the publications cited in findings 10 and 11, supra, to use alkali metal triphosphates or tetraphosphates for softening water.

13. Claims 34 to 39, inclusive, 67 and 68 are unpatentable in view of the prior art.

Conclusions of Law

1. Plaintiffs are not entitled to a patent on application No. 733,392 containing claims 34 to 39, inclusive, 67, 68 and 69 of the said applications, or any of them.

2. The Complaint should be dismissed as to all the claims involved.

EDWARD C. EICHER,
Chief Justice.

* * * * * * * * * *

61 *Judgment*

This cause having come on to be heard and having been tried in open court and argued by counsel for the respective parties upon the pleadings and proofs adduced and submitted to the Court,

It is ADJUDGED this 23rd day of December, 1942, that the complaint in this case be, and the same hereby is dismissed with costs against the plaintiffs.

EDWARD C. EICHER,
Chief Justice.

* * * * * * * * * *

UNITED STATES
COURT OF APPEALS FOR THE
DISTRICT OF COLUMBIA

FILED SEP 14 1943

Joseph W. Stewart

CLERK

BRIEF FOR APPELLEE

In the United States Court of Appeals for the District of Columbia

Appeal No. 8472

Monsanto Chemical Company, appellant

v.

Conway P. Coe, Commissioner of Patents, appellee

APPEAL FROM THE JUDGMENT OF THE DISTRICT COURT OF THE UNITED STATES FOR THE DISTRICT OF COLUMBIA

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In the United States Court of Appeals for the District of Columbia

APPEAL NO. 8472

MONSANTO CHEMICAL COMPANY, APPELLANT
v.
CONWAY P. COE, COMMISSIONER OF PATENTS, APPELLEE

APPEAL FROM THE JUDGMENT OF THE DISTRICT COURT OF THE UNITED STATES FOR THE DISTRICT OF COLUMBIA

BRIEF FOR THE COMMISSIONER OF PATENTS

INTRODUCTION

This is an appeal from the judgment of the District Court of the United States for the District of Columbia (155)[1] dismissing appellant's complaint brought under Section 4915 R. S. (U. S. C., Title 35, Sec. 63) to authorize the Commissioner of Patents to issue to appellant a patent containing claims 34 to 39, inclusive, 67 and 68 of the application of Charles B. Durgin et al., Serial No. 733,392.

APPELLANT'S APPLICATION

The Durgin et al. application (73) relates to the softening of water and discloses the use of fused reaction products of pyro and meta phosphates as treating agents. In one specific example given, monosodium orthophosphate and disodium orthophospate are reacted at about 620° C. In another example phosphoric acid and sodium carbonate are the reactants. The application contains no express mention of triphosphates or tetraphosphates.

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[1] The numbers in parentheses refer to pages in appellant's appendix.

THE HALL ET AL. PATENT NO. 1,903,041

Patent No. 1,903,041 (100) discloses the use of alkali-metal metaphosphates for the treatment of water.

THE HALL PATENT NO. 1,956,515

Patent No. 1,956,515 (111) discloses the use of sodium metaphosphate, pyrophosphate or hexametaphosphate, and of the fused, quickly cooled reaction product of sodium metaphosphate and sodium pyrophosphate, or the fused, quickly cooled reaction product of mono sodium dihydrogren orthophosphate and alkali such as sodium carbonate for the softening of water.

GMELIN'S HANDBUCH

This Gmelin publication (130–132) discloses the substances sodium triphosphate and sodium tetraphosphate, and the methods of preparing them. Similar disclosures are made in the pages of the Zeitschrift publication of 1910 which are reproduced in pages 123 to 130 of appellant's appendix.

APPEALED CLAIMS

The appealed claims appear on pages 4 and 5 of appellant's appendix.

SUMMARY OF ARGUMENT

1. Claims 34 to 39, 67 and 68 are not supported by the original disclosure of the Durgin et al. application here involved.

2. Claims 34 to 39, 67 and 68 are unpatentable in view of the prior art.

ARGUMENT

All the appealed claims have been refused on the ground that they are not supported by the original disclosure of the application here involved. It is to be noted that claims 34 to 39 are copied from the patent to Fiske, No. 2,059,570 (61) and that, in accordance with the settled rule, any doubt as to the right of the applicants to make these claims should be resolved against them (*Lindley* v. *Shepherd,* 58 App. D. C. 31, 24 F. (2d) 606; *Steenstrup* v. *Morton,* 58 App. D. C. 343, 30 F. (2d) 867).

Claims 34 to 39 call for the use of tetraphosphate salts in softening water, and claims 67 and 68 call for the use of triphosphate salts for the same purpose. The lower court's third finding of fact, which is undisputed here, states that the Durgin et al. application "contains no express mention of the use of tetraphosphates or triphosphates for the softening of water," and it is thus clear that the application contains no express basis for any of the appealed claims. It is accordingly incumbent on the appellant to show that the subject matter of the claims is inherent in what is expressly disclosed. This does not mean merely that one following the teaching of the application *might conceivably* practice the invention set forth in the claims; it is essential that this invention should *necessarily* result from following such teaching. This rule is well stated in the decision of the United States Court of Customs and Patent Appeals in *Brand* v. *Thomas,* 25 C. C. P. A. 1053, 96 F. (2d) 301 as follows:

> "Lack of clear disclosure is not supplied by a speculation as to what one skilled in the art might do or might not do if he followed the teaching of the inventor. The disclosure should be clearer than to suggest that one skilled in the art *might* construct the device in a particular manner."

The issue may be most readily understood from the chart introduced by the appellant as exhibit 1 and appearing on page 41 of his appendix. On this chart the entire shaded area represents the range of ingredients which the application suggests as satisfactory and, according to the testimony of the appellant's witness, Reynolds, the area colored yellow may be taken as indicating sodium tetraphosphate (claims 34–39), while the part colored orange indicates sodium triphosphate (claims 67 and 68). This testimony will be accepted as accurate for the purposes of the present argument.

It will be noted that the application does not indicate in any way that either the area colored orange in exhibit 1 or that colored yellow is superior to the remainder of the shaded area, and the optimum percentages for tetraphosphate and triphosphate, which would be in the center of the yellow and orange areas, respectively, are not mentioned at all. It is thus clear that the applicants had no idea that there was any advantage in using either of these substances. They did not mention them expressly and they did not indicate that percentages of ingredients which would produce them were especially desirable. It is true that example one of the application gives a proportion which, theoretically, would be at the extreme edge of the yellow zone, while example two is at an extreme edge of the orange zone. These, however, are theoretical values and there is no testimony to show that the actual carrying out of the express procedure of either example would produce either of the substances claimed. Certainly, since the examples are at the edges of the colored zones it was incumbent on the appellant, if it desired to rely on the specific examples, to show that they fell within these zones. This was not done, since it does not appear that any of the experiments carried out by Reynolds began with the specific materials and percentages set forth in these examples.

The question, therefore, is simply whether an applicant, who discloses a certain range as suitable, without indicating a preference for any particular part of it, is entitled to select a particular portion, constituting one-sixth of the range and claim it as constituting an invention. It seems clear that this question must be answered in the negative. The appealed claims could be held allowable only on the assumption that the specific compositions set forth produced peculiar beneficial results not produced by other compositions of a similar nature, and the consideration for the grant of a patent must be the disclosure to the public of this special advantage. No such disclosure appeared in the Durgin et al. application as filed. There is nothing whatever in the application to teach that either triphosphates or tetraphosphates have any special properties which would make them particularly desirable for water softening, and it is significant that Durgin et al. advanced no claim to these substances until they had learned of such special properties of tetraphosphates from the Fiske patent.

The decision of this Court in *Beckett* v. *Coe,* 98 F. (2d) 332, 69 App. D. C. 51, appears to be in point here. In that case Beckett claimed a particular alloy which, the Court held, "was found within ranges already known" but because "within previously claimed ranges Beckett has found more restricted ones which produce a different alloy from that known to the prior inventors" his claims were held not to be anticipated by the prior disclosures of the broad range. By analogy it would seem that, in the present case, the disclosure by Durgin et al. of a broad range within which both tetraphosphates and triphosphates lie, should not entitle them to present claims specific to these substances.

It is submitted that the appealed claims are drawn to specific substances which, since they are recited as forming the essence of the claimed invention, must be considered critical; and that the disclosure by Durgin et al. of a broad range within which these substances fall, without either naming them or indicating any preference for the portions of the range in which they lie, does not constitute a proper disclosure of the claimed invention.

The appealed claims have also been held unpatentable over the prior art. Before considering the merits of this holding it is advisable to discuss several collateral arguments advanced by the appellant. The first of these is that since claims 34 to 39 have been allowed in the Fiske patent, their patentability should be taken as established. The decision of this Court in *Fessenden* v. *Coe,* 69 App. D. C. 193, 99 F. (2d) 426, is controlling on this point. It was there held that, while the previous allowance of a claim might have persuasive value, it was not controlling. Each of the tribunals passing on this case has been cognizant of the fact that claims 34 to 39 are copied from the Fiske patent, and has given that fact due consideration.

The appellant also urges that the Patent Office has allowed to Durgin et al. claims 62 to 66 of their application, which claims, it is asserted, are broader than those on appeal. Even if this statement were accurate, the allowance of claims 62 to 66 would not be controlling here (*Dyer* v. *Coe,* 125 F. (2d) 192, 75 U. S. App. D. C. 125; *Sharp* v. *Coe,* 125 F. (2d) 185, 75 U. S. App. D. C. 118). Moreover, while claims 62 to 66 are broader than the appealed claims in the sense that they include substances other than triphosphates and tetraphosphates, they are narrower in that they are limited to fusion products of specific starting agents. The appealed claims are drawn broadly to certain triphosphates and tetraphosphates, however prepared and thus include within their scope substances which would not infringe claims 62 to 66. The witness Reynolds (36) testified that tetraphosphates and triphosphates could be prepared by "the fusion of any materials which would lead to the composition." Claims 62 to 66 are limited to specific substances of this character. Moreover, while Reynolds stated that, so far as he knew, triphosphates and tetraphosphates could be prepared only by fusion, the appealed claims are not limited to this but would cover any other method of preparation which is now known or may later be discovered. Claims 62 to 66 are thus, clearly, more limited in some respects than the appealed claims, and their allowance has no bearing on the issue presented here.

The appellant's brief (page 19) contains the statement that "The District Court was not faced with a decision of an administrative tribunal finding that the claims in issue did not involve invention as in *Abbott* v. *Coe*, 109 F. (2d) 449, 71 App. D. C. 195, and other decisions of this Court to like effect. On the contrary, the administrative findings before the Court in the present appeal are explicit that there was invention." It is by no means clear what the basis for this assertion is. The primary examiner, in his statement (142, 143), expressly and at great length held all the appealed claims unpatentable over the prior art. The Board of Appeals (150) stated that "The Examiner's action is affirmed as to claims 34 to 39, inclusive." The action thus affirmed included the rejection on prior art, and the general affirmance acts as an affirmance of all grounds of rejection relied on by the examiner, whether or not they are expressly mentioned in the Board's decision (*In re Wagenhorst,* 20 C. C. P. A. 991, 64 F. (2d) 780; *In re Emanueli,* 21 C. C. P. A. 701, 67 F. (2d) 445; *In re Lilienfeld,* 21 C. C. P. A. 792, 67 F. (2d) 920; *In re Schoenky,* 21 C. C. P. A. 1052, 69 F. (2d) 982). The lower court, therefore, clearly had before it a holding by an administrative tribunal that the appealed claims were unpatentable; and the doctrine of *Abbott* v. *Coe* was applicable.

It will thus be seen that the issue as to the patentability of the appealed claims should be decided strictly on its merits and that unless these claims define a patentable invention they should not be allowed. The rejection is based on either of the two Hall patents, but since No. 1,956,515 is the more pertinent of the two, the other will not be discussed in detail. Hall patent No. 1,956,515 discloses the idea of softening water by the use of various alkali-metal phosphates. Among those listed are metaphosphates, especially hexametaphosphates; trimetaphosphates, trisodium phosphate, and sodium hexametaphosphate mixed with pyrophosphate. The question naturally arises why, if it was old to use these various alkaline phosphates for softening water, it was not obvious to try the similar tetraphosphates and triphosphates, which were admittedly known in the art long prior to any date alleged by Durgin et al. This question has not been satisfactorily answered. The witness Reynolds, although given ample opportunity to answer it (36–39), was both vague and evasive, but finally admitted, in answer to the last question on cross-examination (39) that his only reason for considering that it was not obvious to try tetraphosphates and triphosphates was that trained chemists had not thought of it sooner. This, of course, is not a satisfactory answer. There must be a first time for thinking of everything, no matter how obvious it may be.

It is contended by the appellant that since triphosphates and tetraphosphates show superiority in water softening over unfused mixtures of pyro- and metaphosphates, there was invention in using them. This is not thought to be the case. As was held by this Court in *Naamlooze Vernootschafs* v. *Coe,* 76 U. S. App. D. C. 313, 132 F. (2d) 573, not every new and useful result that is accomplished by experiment is patentable and, if the idea of experimenting with a certain substance is obvious, the fact that the result of the experiment is successful does not render it inventive. This should be clear from the very nature of experiments, since their purpose is to ascertain facts which cannot be certainly forecast. If the result of an experiment could be accurately foreseen, the experiment would be unnecessary. Clearly, therefore, a patent should not be granted whenever the result of an experiment exceeds expectations.

In the present case, moreover, there is no evidence of any startling superiority of tetraphosphates and triphosphates over all prior preparations used for water softening. The tests relied on by the appellant (55) compare these substances only with unfused mixtures of pyro- and metaphosphates. This falls far short of showing unexpected superiority over all the phosphate preparations which had been previously used. It is submitted, therefore, that the idea of using tetraphosphates and triphosphates for water softening was not an inventive one.

It is stated on page 15 of appellant's brief that "Hall patent 1,956,515 was filed subsequent to the filing of applicants' parent application, Ser. No. 438,955, and is therefore not a proper reference against the claims in issue." This statement is incorrect unless application No. 438,955 discloses the subject matter of the appealed claims. The burden of showing this rests strictly on the appellant and, since he has not undertaken to sustain it, it seems unnecessary to discuss the matter in detail here. It should be noted, however, that application No. 438,955 did not, as filed, suggest the use of any of the substances which it discloses, for softening water, but merely disclosed their use for treating boiler water. Each of the appealed claims is limited to the softening of water and any disclosure relied on to support them should, therefore, disclose this feature. However, if it should be held that such disclosure is unnecessary, then the Hall et al. patent, No. 1,903,041, which was granted on an application filed prior to No. 438,955, and which discloses the use of various preparations of the type disclosed by Hall patent No. 1,956,515, in boiler water would provide an effective anticipation of the appealed claims.

There is a further point which should be considered in determining the patentability of the appealed claims in the Durgin et al. application, as distinguished from their abstract patentability. This is the fact that, whatever remarkable and unexpected results are obtained by the use of tetraphosphates and triphosphates, no suggestion of such results is contained in the Durgin et al. application. It seems obvious that an unexpected advantage possessed by a portion only of the range disclosed by the applicants, which advantage apparently was unknown to them, when their application was filed, cannot now form the basis for the allowance to them of claims to this portion. In this respect the situation is similar to that in *Abbott* v. *Coe,* 71 App. D. C. 195, 109 F. (2d) 449, wherein the appellant's case hardening process produced an unexpected result which, however, was not mentioned in the application. In speaking of this the Court said: "This result was highly useful. But it was not claimed or disclosed, and it cannot retroactively turn the adoption of case hardening for other purposes into invention." Similarly, in the present case, the alleged superiority of tetraphosphates and triphosphates, which does not appear to have been suspected by Durgin et al. when they filed their application cannot retroactively justify the allowance to them of the appealed claims.

It should also be noted that Hall patent No. 1,956,515 (page 2, line 60 et seq.) definitely contemplates the use of a fused reaction product of sodium pyrophosphate and sodium metaphosphate, which are the ingredients relied on by appellant as producing tetraphosphate and triphosphate. It follows that Durgin et al. have done no more than change the specific proportions of these ingredients used by Hall, and it is well settled that changes in proportions are unpatentable in the absence of any new or unexpected result (*Allen* v. *Coe,* Court of Appeals D. C., decided April 5, 1943, 57 U. S. P. Q. 136). As previously noted, no such result has been shown in the present case.

CONCLUSION

It is submitted that the appealed claims are not supported by the original disclosure of the Durgin et al. application, No. 733,392, and that they are unpatentable over the prior art. The lower court, therefore, properly dismissed the Complaint in this case, and its action should be affirmed.

Respectfully submitted.

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September 1943.

U. S. GOVERNMENT PRINTING OFFICE: 1943

REPLY BRIEF FOR APPELLANT

IN THE

United States Court of Appeals

DISTRICT OF COLUMBIA.

No. 8472

MONSANTO CHEMICAL COMPANY, *Appellant*,

v.

CONWAY P. COE, COMMISSIONER OF PATENTS,
Appellee.

UNITED STATES
COURT OF APPEALS FOR THE
DISTRICT OF COLUMBIA

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IN THE

United States Court of Appeals

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No. 8472.

MONSANTO CHEMICAL COMPANY, *Appellant,*
v.
CONWAY P. COE, COMMISSIONER OF PATENTS,
Appellee.

REPLY BRIEF FOR APPELLANT.

It is regretted that erroneous and misleading statements in the brief for the Commissioner of Patents require the filing of a reply brief.

On page 2 of appellee's brief, in discussing Gmelin's Handbuch, appellee fails to point out that, not only does this publication disclose the substances sodium triphosphate and sodium tetraphosphate and the methods of preparing them, but the methods there disclosed for the preparation of these compounds are identical with the methods disclosed by applicants for preparing their water-treating materials.

The following evidence and testimony in the record proves beyond any reasonable question that the substances which applicants disclose for the treatment of water are the substances known to the art by the names used in the claims in issue:

Reference	Appendix Page	Abstract
Parravano et al.	125	". . . we obtain by fusing pyrophosphate with metaphosphate in various proportions, the different types of polyphosphates."
Gmelin	130	"F. Schwarz . . . obtained from the melt of $Na_4P_2O_7$ and $NaPO_3$ . . . various crystallized polyphosphates".
Gmelin	131	"$Na_5P_3O_{10}$ . . . We heat a mixture . . . of . . . $Na_4P_2O_7$ and hexametaphosphate to the melting point . . . According to both authors it is . . . the sodium salt of triphosphoric acid, $H_5P_3O_{10}$."
Gmelin	131	"$Na_6P_4O_{13}$ . . . We heat a mixture of hexametaphosphate with . . . $Na_4P_2O_7$ . . . there will be formed the hydrous salt of the above substance".
Dammer	43	"Tetraphosphoric acid, $H_6P_4O_{13}$. The Na salt . . . is formed by melting together $NaPO_3$ and $Na_4P_2O_7$ or by melting together $NaPO_3$ and Na_3PO_4 . . . according to: $Na_6P_6O_{18} + 3Na_4P_2O_7 = 3Na_6P_4O_{13}$ and $Na_6P_6O_{18} + 2Na_3PO_4 = 2Na_6P_4O_{13}$."
Ephraim	45	"The tri- and tetraphosphoric acids, $H_5P_3O_{10}$ and $H_6P_4O_{13}$, are not known in the free state, but their sodium salts are obtained by fusing together suitable quantities of sodium pyro- and metaphosphates".
Mellor	49	"Polyphosphoric Acids" "Salts of some of these acids were made by Fleitmann and Henneberg, P. Gluhmann, F. Schwarz and M. Stange, by heating metaphosphates with pyro-phosphate or orthophosphates. On cooling a fused mixture of anhydrous sodium pyrophosphate . . . with sodium metaphosphate, which has been kept at a bright red-heat . . . a crystalline mass of sodium triphosphate, $Na_5P_3O_{10}$ is obtained: $Na_4P_2O_7 + NaPO_3 = Na_5P_3O_{10}$".
Mellor	50	"T. Fleitmann and Henneberg also prepared sodium tetraphosphate, $Na_6P_4O_{13}$—representing tetraphosphoric acid, $H_6P_4O_{13}$ . . . by melting together a mixture of eq. amounts of sodium hexametaphosphate, $Na_6P_6O_{18}$, and sodium pyrophosphate: $Na_6P_6O_{18} + 3Na_4P_2O_7 = 3Na_6P_4O_{13}$ . . ."
Reynolds	17	"The conclusion appears obvious that they (sodium tetraphosphate and sodium triphosphate) are prepared by the method disclosed by the specification of the Durgin et al. application . . .".

On page 4 of appellee's brief occurs the statement:

> "It will be noted that the application does not indicate in any way that either the area colored orange in Exhibit 1 or that colored yellow is superior to the remainder of the shaded area, and the optimum percentages for tetraphosphate and triphosphate, which would be in the center of the yellow and orange areas, respectively, are not mentioned at all."

This is an erroneous and misleading statement, first, because specific examples of compositions within the orange and yellow colored areas, respectively, are set forth in applicants' original specification and, second, because the issue is not whether "either the area colored orange in Exhibit 1 or that colored yellow is superior to the remainder of the shaded area", but whether the substances in the colored areas are superior to the materials proposed for water treatment by the prior art.

As to the first point, Dr. Reynolds testified that materials in the yellow area contain 85 per cent or more of tetraphosphate (App. p. 32) and that materials in the orange area contain 85 per cent or more of triphosphate (App. p. 33). Example 1 of applicants' specification (App. p. 75) is a composition within the yellow range, and Example 2 (App. p. 76) is a composition within the orange range. Moreover, appellee entirely overlooked the fact that Fig. 5 of the drawing of the application, upon which Exhibit 1 is based, is itself a graphic disclosure of compositions throughout these ranges and taken with the other figures and the written description provides a full description of the composition and properties of the compositions throughout these ranges.

The second point may be more particularly discussed with reference to the case of *Becket* v. *Coe* cited on page 6 of appellee's brief. In the Becket case, the inventor was claiming a particular alloy selected from within a range of previously known alloys. This Court held that the claims were not anticipated by the prior disclosures of the broader ranges.

If the prior disclosures of the broader range did not prevent the allowance of claims to a narrower range to Becket, it is hard to see why the disclosure of a broader range in applicants' own specification should prevent the allowance of claims to a narrower range to applicants.

Moreover, there is no contention here, nor is appellant required to show, that the products of the specific claims in issue have a special superiority over the broader range of compositions covered by the allowed claims. It is enough if they have, as the record clearly shows they have, the same superiority over the prior art materials as the broader range of compositions.

On page 5 of appellee's brief, it is stated that "there is no testimony to show that the actual carrying out of the express procedure of either example would produce either of the substances claimed". This statement is incorrect. For example, sample No. 26 of Exhibit 7 (App. p. 54) is a repetition of Example 2 of the specification. Exhibit 11 (App. p. 58) includes the X-ray diagram of sample No. 26 in comparison with the X-ray diagrams of samples 6, 12 and 18. The witness Reynolds testified (App. p. 28) that sample No. 11 is illustrative of the material referred to in the literature as sodium triphosphate and that the X-ray diagrams show identity of samples 11 and 26. Note also Reynolds' unequivocal statement at the bottom of page 17 and the top of page 18 of the Appendix.

On page 6, first paragraph, of appellee's brief it is alleged that applicants did not advance claims to the tri- and tetra-phosphates until the Fiske patent issued. This statement is misleading and begs the question at issue. Applicants were continuously claiming, and have been allowed, claims to the use of the substances defined by other language. Applicants merely copied the *terminology* of the claims of the Fiske patent for the purpose of establishing priority of invention of this subject matter under the rules of the Patent Office.

On page 7, last four lines and the first paragraph on page 8, appellee argues that the claims on appeal are not limited to any particular method by which the tri- and tetra-phosphates may be prepared. Applicants' specification discloses at least two distinct methods for preparing these materials as well as the general statement that the fundamental reaction underlying these methods is the reaction between metaphosphates and pyrophosphates. Fiske, on the other hand, to whom the tetraphosphate claims have been allowed, set forth no specific method for preparing these materials. All Fiske did was to state that the compounds were old, and that the method for preparing them is old.

On page 9, second paragraph, appellee asks why it involves invention to use tetra- and tri-phosphates in view of the fact that other phosphates have previously been used to soften water. The Commissioner has already answered this question by issuing the Fiske patent. The Board of Appeals has answered the question by allowing the broader claims of appellant's application. Other answers to this question are found on pages 15 and 16 of appellant's brief.

On page 10 of appellee's brief it is stated that "there is no evidence of any startling superiority of tetraphosphates and triphosphates over all prior preparations used for water softening". This obviously sets up an unjustifiable requirement. Applicants' original disclosure (e. g. at App. p. 83) and the data illustrated by Exhibit 8 (App. p. 55) show the unpredictable superiority of tetraphosphates and triphosphates over the only prior art materials cited by the Patent Office. Nothing more is required of applicants than to meet the prior art relied on by the Patent Office. As the record shows, the pyro- and metaphosphates are the only phosphates which the Commissioner of Patents at any time has contended were pertinent to applicants' invention (See decision of the Board of Appeals, App. p. 149).

Beginning at the bottom of page 10 of appellee's brief, it is contended that Hall patent 1,956,515 is a proper reference because applicants' parent application Ser. No. 438,955 (Exhibit 16, App. p. 64) did not disclose the use of the new compounds for "softening water" but merely disclosed their use "for treating boiler water". The treatment of boiler water is water softening. As the Hall patent points out, water softening is the reduction of the calcium or magnesium ion content of the water. Applicants' parent application uses the equivalent terminology "to precipitate the positive ion of various undesirable salts of the alkaline earth group metals from solution" (App. p. 65). Appellee's contention is therefore merely a misleading statement without any basis in fact. Boiler water treatment to remove ions of alkaline earth metals as disclosed in applicants' parent application is water softening and the implication to the contrary in appellee's brief is not merely unjustified but unjust and out of place in a brief on behalf of the Commissioner of Patents.

It is to be pointed out, moreover, that the Hall patent 1,956,515 does not disclose any compositions which contain either tri- or tetraphosphates. The Hall patent is directed to the use of *alkali metal metaphosphates* for water softening. At page 2, line 60 of the patent, it is stated that to counteract acidity of the metaphosphate "a small amount of sodium pyrophosphate" may be added. Further, in lines 77-80 of page 2 of the patent, Hall says:

> "The amounts of such neutralizing agents are relatively small and my water softener consists principally of sodium metaphosphate . . .".

Contrary to the implication in appellee's brief at page 11, the earlier Hall patent 1,903,041 does not contain any reference to fusion of alkaline materials with metaphosphate to form a small amount of pyrophosphate as set forth in lines 60 and following of page 2 of the later Hall patent.

The weakness of appellee's position is highlighted by the reliance on misleading, erroneous and unjustified statements in appellee's brief. The judgment of the District Court is clearly erroneous and should be reversed.

Respectfully,

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